

15

NASA Contractor Report 3876

Theoretical Studies of the Ignition and Combustion of Silane-Hydrogen-Air Mixtures

Wallace Chinitz

GRANT NAG1-18
FEBRUARY 1985

NASA

NASA Contractor Report 3876

Theoretical Studies of the Ignition and Combustion of Silane-Hydrogen-Air Mixtures

Wallace Chinitz

The Cooper Union Research Foundation

New York, New York

Prepared for
Langley Research Center
under Grant NAG1-18



National Aeronautics
and Space Administration

Scientific and Technical
Information Branch

1985

SUMMARY

A chemical kinetic mechanism is proposed for the combustion of silane-hydrogen-oxygen-nitrogen mixtures in the initial temperature range from 800K to 1250K and pressure range from 0.5 to 1.35 atm. The mechanism yields results which are in agreement with published ignition delay times obtained from shock tube experiments. Comparisons between the results obtained using the proposed mechanism and that set forth in ref. 6 reveal that the former predicts appreciably shorter ignition delay times, but a flame blowout envelope which is shifted so as to decrease the stable flame region. Over much of the thermodynamic range examined, the mechanism predicts long reaction times. A three-step global mechanism is proposed which closely models the ignition phase of SiH_4 - H_2 - air combustion; however, the reaction phase is less well reproduced by the global model. The necessity for additional experimental data to further assess the proposed models is stressed.

INTRODUCTION

The pyrophoric nature of mono-silane (SiH_4 , also called silane) over a wide range of pressures and temperatures has been well established (e.g., refs. 1 and 2). Its pyrophoricity has led to recent work using silane as a fuel additive to enhance the ignition, combustion and flame stabilizing properties of hydrogen (ref. 3) and hydrocarbons (ref. 4) burning in air.

In order to better understand its behavior at the conditions encountered in practical devices, such as the combustion of a SCRAMJET engine (ref. 3), and to be able to predict a priori its behavior at conditions which cannot be readily achieved in the laboratory, a reliable chemical kinetic mechanism is required. The first attempt at the formulation of such a mechanism is in ref. 3. It was shown subsequently (ref. 5), however, that the mechanism in ref. 3 yields predicted ignition delay times which are about five times longer than those obtained experimentally in shock tube tests. As a result, an alternative mechanism was developed in ref. 6 which predicted ignition delay times which were in agreement with the shock tube data.

The mechanism in ref. 6 postulates that silane pyrolysis



along with its direct oxidation



are the initiating reactions. An examination of the magnitudes of the rate constants used in the mechanism of ref. 6 indicates that reaction (1), along with the extremely rapid subsequent oxidation

of SiH_2



are principally responsible for the disappearance of silane at SCRAMJET engine operating conditions.

Herein, an alternative chemical kinetic mechanism is proposed which closely models methane oxidation (Section 2). Predictions of ignition delay and combustion times (Section 3) and blowout-limit behavior (Section 4) are presented using the proposed mechanism. Comparisons with the results predicted using the mechanism in ref. 6 reveal substantially different behavior over most of the conditions examined. A global chemical kinetic mechanism is proposed in Section 5 and the recommendations in Section 6 may help to resolve the observed differences between the proposed mechanism.

SYMBOLS

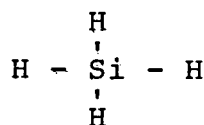
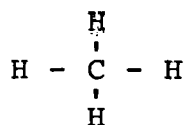
k_f	forward rate coefficient (see Table I)
\dot{m}	mass flow rate (see Figs. 10-16), g/sec
p	pressure, atm
T	temperature, K
t	time, sec
V	reactor volume (see Figs. 10-16), cm^3
X	percent by volume of silane in the fuel
R	universal gas constant (see Table I)
ϕ	equivalence ratio, ratio of fuel (silane plus hydrogen)-to-air divided by the stoichiometric fuel-to-air ratio

Subscripts:

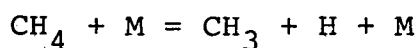
af	adiabatic flame
ig	ignition
R	reaction
0	initial
RES	residence time

CHEMICAL KINETIC MECHANISM

As was pointed out in ref. 3, "silicon is a member of the Group IV elements appearing directly below carbon on the periodic table." As a result, the silane and methane molecules are analogous:



This chemical-structural similarity may imply that a similar chemical kinetic mechanism for the oxidation of the two compounds exists. The principal initiating reaction in the oxidation of methane is hydrogen abstraction (refs. 7 and 8):



with a forward rate coefficient of $k_f = 2 \times 10^{-17} \exp(-88,421.5/RT)$. By analogy, the reaction

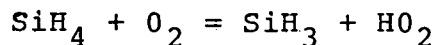


is proposed, having a forward rate coefficient $k_f = 2 \times 10^{-17} \exp(-59,000/RT)$. The activation energy was obtained by scaling the value for the equivalent methane reaction using the respective C-H and Si-H bond energies.

In methane mechanisms (refs. 7 and 8), $\text{CH}_4 + \text{R}$ reactions are proposed, in which $\text{R} = \text{O}, \text{H}$ and OH . Similarly, a sequence of $\text{SiH}_4 + \text{R}$ reactions are proposed here, wherein $\text{R} = \text{O}, \text{H}, \text{OH}, \text{SiH}_3$ and HO_2 (Table I). The reaction with SiH_3 is suggested by the work in ref. 9 and the rate coefficient for the $\text{SiH}_4 + \text{SiH}_3$ reaction in Table I is that for the $\text{SiH}_4 + \text{CH}_3$ reaction in ref. 9. The

$\text{SiH}_4 + \text{HO}_2$ reaction and rate coefficient are proposed in ref. 6.

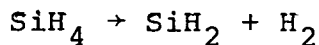
The pyrophoric nature of silane suggests the likelihood of the direct attack on SiH_4 by O_2 molecules. In ref. 6, this is treated as a hydrogen abstraction:



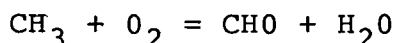
It is suggested here that this reaction may, in fact, result in the formation of water:



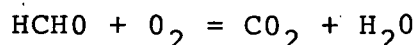
As written, reaction (ii) may, in fact, be semi-global in nature, being analogous to the thermal decomposition reaction



in ref. 6 and the reactions



in ref. 7 and



in ref. 8. That is, each of the above reactions may embody a set of rapidly-occurring elementary reactions whose overall effect, relative to the rates of the remaining reactions in the mechanism, is summarized by the reaction as written. The pre-exponential factor for reaction (ii) was estimated from collision theory and the activation energy was obtained from a Semenov-type correlation (ref. 10).

The remaining reactions in Table I, along with their rate coefficients, were assembled from refs. 3 and 6, with one important exception. The pre-exponential factor for the reaction



is specified in ref. 6 as $8.6 \times 10^{14} \text{ cm}^3/\text{mole-s}$, a value which exceeds the maximum value predicted by collision theory. The value used in this study, $1.72 \times 10^{14} \text{ cm}^3/\text{mole-s}$, is less than the maximum collision theory value.

Comparisons are made in figs. 1 and 2 between the ignition delay times determined experimentally in a shock tube (ref. 5) and those predicted by the mechanism in Table I. The agreement in figs. 1 and 2 is regarded as quite good. As a result, additional studies were undertaken using the mechanism in Table I to assess the ignition, combustion and flame stabilization behavior of silane-air and silane-hydrogen-air mixtures.

IGNITION DELAY AND COMBUSTION TIME CALCULATIONS

The computer program described in ref. 11 was run in its constant pressure streamtube mode to determine ignition delay and combustion times. Herein, the ignition delay time t_{ig} is taken to be the time required to go from the initial state of the fuel-air mixture to the time when the reacting mixture temperature reaches $T_0 + 0.05 \Delta T$, where T_0 is the initial temperature, $\Delta T = T_{af} - T_0$, and T_{af} is the adiabatic flame temperature. The reaction time t_R is defined as the difference between the time required to reach $T_0 + 0.95 \Delta T$ and the ignition delay time. The sum of these two times (i.e., the time required to go from the initial state T_0 to $T_0 + 0.95 \Delta T$) is referred to as the overall combustion time.

Ignition delay times as a function of reciprocal initial temperature for various silane-hydrogen fuel mixtures are shown in figs. 3 and 4 for one atmosphere and equivalence ratios of one and one-half, respectively. The equivalence ratio is the overall fuel (silane plus hydrogen)-to-air ratio divided by the stoichiometric fuel-to-air ratio. In these figures, silane concentrations range from zero percent (pure H_2) to 100 percent (by volume). The substantial reduction of t_{ig} , even with as little as 2% SiH_4 is apparent, particularly at the lower initial temperatures. Increasing the fuel silane concentration from 2% to 20% results in a further decrease of t_{ig} by about one order-of-magnitude. However, further increases in the fuel silane concentration result in relatively small additional reductions of t_{ig} .

The results of ref. 6 are also presented in figs. 3 and 4.

Except for 2% silane at high temperatures, the mechanism proposed here predicts appreciably lower ignition delay times. For example, for 20% SiH_4 /80% H_2 , $T_0 = 800\text{K}$, $p = 1 \text{ atm}$, $\phi = 1.0$, the predicted t_{ig} is nearly one order-of-magnitude lower than that predicted by the mechanism of ref. 6. These substantial differences in the results predicted by the two mechanisms at the conditions specified in figs. 3 and 5 will permit an assessment to be made of the mechanisms when additional data become available.

Fig. 5 illustrates the effect of increasing equivalence ratio on the ignition delay times of pure silane at one atmosphere. Although it is clear that for some value of $\phi \gg 1$, the pyrolysis mechanism represented by eqs. (1) and (3) becomes important, the results shown in fig. 5 were obtained using the mechanism proposed here (Table I). Over the initial temperature range examined (800 to 1250K), the t_{ig} is reduced by about a factor of three as ϕ is increased from 1 to 4. However, the mechanism predicts that little additional reduction of t_{ig} is achieved by increasing the equivalence ratio above 4.

Fig. 6 shows the effect of pressure on t_{ig} at $\phi = 1$. For all quantities of silane in the fuel (between 2% and 100%), reducing the pressure from one atmosphere to one-half atmosphere about doubles the ignition delay time in the initial temperature regime examined.

On the basis of similar studies with pure hydrogen, it was anticipated that under many thermodynamic conditions, the reaction time would be substantially longer than the ignition delay time; hence, t_R would become rate-controlling. To assess this, t_R was ascertained for many of the cases shown in figs. 3 - 6. Fig. 7

presents results for $p = 1 \text{ atm}$, $\phi = 1$. At these conditions, little difference was found in t_R using 2% and 20% silane in the fuel. However, appreciably lower values of t_R (ranging from one-half to one order-of-magnitude) were calculated for pure silane. Comparing these results with those for t_{ig} in fig. 7, the following conclusions may be drawn:

- . For 2% silane, t_{ig} exceeds t_R at low temperatures, while the reverse is the case at higher temperatures. The cross-over occurs at about 890K.

- . For 20% silane, t_{ig} is appreciably shorter than t_R , ranging from about a factor of 6 lower at $T_0 = 800\text{K}$ to about two orders-of-magnitude lower at $T_0 = 1250\text{K}$.

- . For pure silane, t_{ig} is lower than t_R over the initial temperature range examined, ranging from about a factor of 2 lower at $T_0 = 800\text{K}$ to about an order-of-magnitude lower at $T_0 = 1250\text{K}$.

Values for reaction times at $\phi = 0.5$, $p = 1 \text{ atm}$ are shown in fig. 8. In this case, relatively little difference is observed in the calculated t_R values in going from 2% silane to 100% silane. As in fig. 7, t_{ig} exceeds t_R only for 2% silane at temperatures between 800K and 895K, while t_{ig} is significantly lower than t_R for the 20% and 100% silane fuels over the initial temperature range examined.

Figure 9 shows t_R values for $\phi = 1$, $p = 0.5 \text{ atm}$. Here, the 2% and 20% silane fuels exhibit virtually the same reaction times, while t_R for pure silane is substantially lower. Once again, only for the 2% silane fuel is an initial temperature range encountered

wherein $t_{ig} > t_R$ (in this case, $800K \leq T_0 \leq 850K$). For the 20% and 100% silane cases, t_{ig} is appreciably less than t_R over the range examined.

These reaction time results clearly indicate the necessity for dealing with both ignition delay and reaction times. Over most of the conditions examined, t_R is substantially greater than t_{ig} and, thus, is the rate-controlling phenomenon in the approach to the adiabatic flame temperature.

It is frequently useful to have available a correlation of the t_{ig} and t_R data discussed above. The form of the correlation often used was first proposed in ref. 12. For the data presented here, these correlations for the 20% $SiH_4/80\% H_2$, $\phi = 1$, cases are:

$$t_{ig} = 1.775 \times 10^{-9} p^{3.146} \exp(8254/T_0) \text{ sec}$$

valid to $\pm 2\%$, and

$$t_R = \frac{1.206 \times 10^{-3} \exp(-1.711 \times 10^{-3} T_0)}{p^{1.554}} \text{ sec}$$

valid to $\pm 10\%$

PERFECTLY-STIRRED REACTOR CALCULATIONS

Engine combustion chambers generally provide regions in which the combusting fuel-air mixture may be stabilized subsequent to ignition. These regions generally are the wake-like regions behind bluff bodies, struts and rearward-facing steps, or the recirculation regions in the vicinity of fuel injection locations. An assessment of the flame-holding capabilities of various fuel-air mixtures may be made by assuming that these regions may be modeled as perfectly-stirred reactors (PSR, see, for example, ref. 8). The perfectly-stirred reactor computer program used for the studies reported herein was that discussed in ref. 13.

A typical result is shown in fig. 10 which is the standard blowout limit representation first proposed in ref. 14; i.e., equivalence ratio ϕ as a function of the ratio of the mass flow rate of reactants into the reactor to the reactor volume, \dot{m}/V . Since $\dot{m}/V \sim t_{\text{RES}}^{-1}$, where t_{RES} is the minimum residence time required to ensure a stable flame (i.e., the minimum time an element of mass must reside in the reactor to prevent flame blowout), fig. 10 indicates that the mechanism in ref. 6 predicts a larger stable flame region (i.e., a decreased likelihood of flame blowout over a wider range of conditions) than does the mechanism proposed herein. As was the case with the predicted t_{ig} values discussed in the previous section, this difference in predicted results could provide a basis for assessing the two mechanisms should experimental PSR results become available. It

should be noted in fig. 10 that, in contrast with such fuels as hydrogen and the hydrocarbons, both mechanisms predict a maximum \dot{m}/V value at a ϕ of about 2.5, rather than $\phi = 1$. It is not possible to assess, at this time, whether this is physically reasonable behavior, or is attributable to either an anomaly in the thermochemical data used in the computer program, or in the method for determining blowout, or that the reaction mechanism is incomplete.

Blowout limit curves at one atmosphere for pure hydrogen, 20% silane/80% hydrogen and 100% silane fuels are shown in figs. 11 and 12 for initial reactant temperatures of 300K and 600K, respectively. Similar conclusions may be drawn in both instances:

. Pure silane flames are most stable at equivalence ratios exceeding unity. However, for $\phi \approx 1.0$ ($T_0 = 300K$) and $\phi \approx 0.8$ ($T_0 = 600K$), pure hydrogen flames provide greater flame stability.

. In general, the 20% SiH_4 /80% H_2 are less stable than the neat fuels, except for the region above $\phi \approx 1.5$ ($T_0 = 600K$), where it is about equivalent to hydrogen, and the region below $\phi \approx 0.7$, where it is about equivalent to silane.

These conclusions suggest that in engine configurations in which 20% SiH_4 is supplied to promote hydrogen ignition, pure hydrogen should be used to ensure flame stabilization subsequent to ignition.

The results of figs. 11 and 12 are presented in terms of minimum required residence times (rather than \dot{m}/V) in figs. 13 and 14.

Conclusions similar to those discussed in connection with figs. 11 and 12 may be drawn from figs. 13 and 14. The reduction in the stable flame region resulting from a pressure decrease from 1.0 atm to 0.5 atm is shown in figs. 15 and 16. As may be seen in fig. 16, the minimum required residence time about doubles in going from 1.0 atm to 0.5 atm.

A GLOBAL SILANE - HYDROGEN - AIR MECHANISM

Considerations of computer run times and computer storage limitations frequently require the use of a global or quasi-global chemical kinetic mechanism. This is particularly true when developing or using codes describing time-dependent, multi-dimensional and/or turbulent flows (e.g., refs. 8, 15 and 16). The following three-step global mechanism is proposed for the mechanism proposed herein:



The forward reaction rate coefficients recommended are:

$$k_{f,4} = \frac{(0.95234 \phi + 4.4762 \phi^{-1} - 4.4286)}{p^{5.644}} \cdot 10^{15} \cdot$$

$$T^{2.30} \exp (-19350/RT)$$

$$k_{f,5} = 5.0 \times 10^{10} T^{2.80} \exp (-14000/RT)$$

$$k_{f,6} = \frac{(2.3829 \phi + 76.190 \phi^{-1} - 3.5714)}{p^{1.415}} \cdot 10^6 \cdot$$

$$\left(\frac{X}{20}\right)^{0.574} T^{3.29} \exp (-16500/RT)$$

In the above, X represents the percent by volume of silane in the initial fuel mixture. The proposed ranges of validity of this global model are:

$$0.5 \leq p \leq 1.0 \text{ atm}$$

$$0.5 \leq \phi \leq 4.0$$

$$2\% \leq x_{\text{SiH}_4} \leq 20\% \text{ SiH}_4$$

$$800\text{K} \leq T_0 \leq 1250\text{K}$$

Typical results using the proposed global model are presented in figs. 17 - 21, wherein the results are compared with those obtained using the complete mechanism (Table I). Over the range of conditions examined, the global model well represents the ignition phase. However, the subsequent approach to the adiabatic flame temperature is less well represented. Studies employing global reaction models in large-scale computer codes suggest that replication of the ignition period is of principal importance in obtaining acceptable results with global models. Hence, use of the proposed model should result in an adequate representation of the combustion chemistry in such large-scale computer programs.

CONCLUDING REMARKS

A chemical kinetic mechanism has been developed for the oxidation of silane which predicts ignition delay times in agreement with published shock tube data (ref. 5). This mechanism differs from one already proposed (ref. 6) primarily in the assumed initiating reactions, although other differences, discussed herein, exist as well. When the two mechanisms are compared, the one proposed here generally predicts substantially shorter ignition delay times for silane-hydrogen-air combustion over most of the range of thermodynamic conditions examined. On the other hand, the proposed mechanism predicts a reduced flame-stabilizing capability for silane when compared with the mechanism in ref. 6.

These results point to the importance of additional experiments to provide the data necessary to deduce the mechanism which most closely models the data. These experiments include additional shock tube tests encompassing a wider range of data than that in ref. 5, steady-flow reactor experiments similar to those in ref. 17 but without the interfering heterogeneous reactions, and stirred reactor experiments similar to those in ref. 14 to determine flame stability limits.

The generally lengthy reaction times predicted by the mechanism should be noted. Since the proposed mechanism is quite similar to that in ref. 6 beyond the reaction initiation stage, the latter mechanism is likely to predict long reaction times as well.

REFERENCES

1. Merryman, Earl L.; and Levy, Arthur: The Rates of Hydrogen Release in Silane-Air Systems. Battelle Columbus Laboratories, Columbus, Ohio, Nov. 1980.
2. Crince, William J.: Effects of Releases of Silane Mixtures in Ambient Air. Hazards Research Corp. Report 4007, Denville, N.J., Dec. 1978.
3. Beach, H. L., Jr.; Mackley, E. A.; Rogers, R. C.; and Chinitz, W.: Use of Silane in Scramjet Research. 17th JANNAF Combustion Meeting, Volume I, Debra Sue Eggleston, ed., CPIA Publ. 329 (Contract N00024-78-C-5384), Appl. Phys. Lab., Johns Hopkins Univ., Nov. 1980, pp. 639-659.
4. Urtiew, P. A.; Lee, E. L.,; and Walker, F. E.: Free Radicals and Fuel-Air Explosion Initiation. Lawrence Livermore Lab., Livermore, CA., Rept. UCRL-52007, 1976.
5. McLain, Allen G.; Jachimowski, Casimir J.; and Rogers, R. Clayton: Ignition of $\text{SiH}_4\text{-H}_2\text{-O}_2\text{-N}_2$ Behind Reflected Shock Waves. NASA TP-2114, 1983.
6. Jachimowski, Casimir J.; and McLain, Allen G.: A Chemical Kinetic Mechanism for the Ignition of Silane/Hydrogen Mixtures. NASA TP-2129, 1983.
7. Bowman, C. T.; and Seery, D. J.: Investigation of NO Formation Kinetics in Combustion Processes: The Methane-Oxygen-Nitrogen Reaction. Emissions from Continuous Combustion Systems, Plenum Press, NY, 1972, pp. 123-139.
8. Edelman, R. B.; and Harsha, P. T.: Some Observations on Turbulent Mixing with Chemical Reactions. Turbulent Combustion, Lawrence A. Kennedy, ed., AIAA Progress in Astronautics and Aeronautics, vol. 58, 1978, pp. 55-102.
9. Arthur, N. L.; and Bell, T. N.: An Evaluation of the Kinetic Data for Hydrogen Abstraction from Silanes in the Gas Phase. Rev. of Chem. Intermediates, vol. 2, 1978, pp. 37-74.
10. Chinitz, W.; and Baurer, T.: An Analysis of Nonequilibrium Hydrocarbon/Air Combustion. Pyrodynamics, vol. 4, no. 2, Apr. 1966, pp. 119-154.
11. McLain, Allen G.; and Rao, C. S. R.: A Hybrid Computer Program for Rapidly Solving Flowing or Static Chemical Kinetic Problems Involving Many Chemical Species. NASA TM X-3403, 1976.

12. Pergament, Harold S.: A Theoretical Analysis of Non-Equilibrium Hydrogen-Air Reactions in Flow Systems. AIAA Paper No. 63-113, Apr. 1963.
13. Rogers, R. Clayton; and Weidner, Elizabeth H.: Numerical Predictions of Residence Times Behind a Rearward Facing Step With Transverse Injection. 20th JANNAF Combustion Meeting, Volume I, Debra Sue Eggleston, ed., CPIA Publ. 383 (Contract N00024-83-C-5301), Appl. Phys. Lab., Johns Hopkins Univ., Oct. 1983, pp. 635-651.
14. Longwell, J. P.; and Weiss, M. A.: Flame Stability in Bluff Body Recirculation Zones. Indust. and Engrg. Chem., vol. 45, 1953, pp. 1629-1633.
15. Rogers, R. C.; and Chinitz, W.: Using A Global Hydrogen-Air Combustion Model in Turbulent Reacting Flow Calculations. AIAA J., vol. 21, no. 4, Apr. 1983, pp. 586-592.
16. Menon, S.; Anderson, J. D., Jr.; and Pai, S. I.: Stability of a Laminar Premixed Supersonic Free Shear Layer with Chemical Reactions. Int'l J. Engrg. Sci., vol. 22, no. 4, 1984, pp. 361-374.
17. Strater, K.: Controlled Oxidation of Silane. RCA Review, vol. 29, 1968, pp. 618-629.

TABLE I

SILANE OXIDATION MECHANISM*

Reaction				A	n	E
M	SiH ₄	=	SiH ₃ + H	2.00E+17	0.	59000.
SiH ₄	+ SiH ₃	=	2 SiH ₃ + H	7.76E+11	0.	6980.
SiH ₄	+ O ₂	=	SiH ₂ O + H ₂ O	2.00E+14	0.	19600.
SiH ₄	+ H	=	SiH ₃ + H ₂	2.88E+13	0.	2650.0
SiH ₄	+ O	=	SiH ₃ + OH	4.10E+12	0.	1580.0
SiH ₄	+ OH	=	SiH ₃ + H ₂ O	8.64E+12	0.	95.000
SiH ₄	+ H ₂ O	=	SiH ₃ + H ₂ O ₂	3.00E+12	0.	5600.
SiH ₃	+ O ₂	=	SiH ₂ O + OH	1.72E+14	0.	11430.
SiH ₃	+ O	=	SiH ₂ O + H	1.30E+14	0.	2000.
SiH ₃	+ OH	=	SiH ₂ O + H ₂	5.00E+12	0.	0.0
M	+ SiH ₂ O	=	HSiO + H	5.00E+16	0.	76600.
SiH ₂ O	+ H	=	HSiO + H ₂	3.30E+14	0.	10500.
SiH ₂ O	+ O	=	HSiO + OH	1.80E+13	0.	3080.
SiH ₂ O	+ OH	=	HSiO + H ₂ O	7.50E+12	0	170.
SiH ₂ O	+ O ₂	=	HSiO + H ₂ O ₂	3.95E+14	0.0	29500.
SiH ₂ O	+ H ₂ O	=	HSiO + H ₂ O ₂	1.00E+12	0.	8000.
M	+ HSiO	=	H + SiO	5.00E+14	0.	29000.
HSiO	+ H	=	SiO + H ₂	2.00E+14	0.	0.00
HSiO	+ O	=	SiO + OH	1.00E+14	0.	0.00
HSiO	+ OH	=	SiO + H ₂ O	1.00E+14	0.	0.00
HSiO	+ O ₂	=	SiO + H ₂ O ₂	1.20E+14	0.0	3795.
SiO	+ O ₂	=	SiO ₂ + O	1.00E+13	0.	6500.
SiO	+ OH	=	SiO ₂ + H	4.00E+12	0.	5700.
SiO	+ O	=	SiO ₂ + M	2.50E+15	0.	4370.
M	+ O ₂	=	O + O	7.2E18	-1.	117908.
M	+ H ₂	=	H + H	5.5E18	-1	103298.
M	+ H ₂ O	=	H + OH	5.2E21	-1.5	118000.
H	+ O ₂	=	H ₂ O + M	2.3E15	0.	-800.
M	+ H ₂ O ₂	=	OH + OH	1.2E17	0.	45500.
O	+ H	=	OH + M	7.1E18	-1.	0.
H ₂ O	+ O	=	OH + OH	5.8E13	0.	18000.
H ₂	+ OH	=	H ₂ O + H	2.0E13	0.	5166.
O ₂	+ H	=	OH + O	2.2E14	0.	16800.
H ₂	+ O	=	OH + H	7.5E13	0.	11099.

TABLE I - Continued

SILANE OXIDATION MECHANISM*

<u>Reaction</u>					<u>A</u>	<u>n</u>	<u>E</u>
H2	+	O2	=	OH	1.0E13	0.	43000.
H	+	H02	=	H2	2.4E13	0.	695.
H	+	H02	=	OH	2.4E14	0.	1887.
H2O	+	O	=	H	5.8E12	.5	57000.
O	+	H02	=	OH	5.0E13	0.	1000.
OH	+	H02	=	O2	3.0E13	0.	0.
H02	+	H2	=	H	7.3E12	0.	18677.
H2O2	+	H	=	OH	3.2E14	0.	8950.
H02	+	OH	=	O	5.2E10	.5	21062.
H02	+	H2O	=	OH	2.8E13	0.	32785.
H02	+	H02	=	H2O2	2.0E12	0.	0.

* The coefficients are for the rate coefficient in the forward direction written in the form $k_f = AT^n \exp(-E/RT)$, where A is in $\text{cm}^3/\text{mole-s}$ for bimolecular reactions, and $\text{cm}^6/\text{mole}^2\text{-s}$ for termolecular reactions. The activation energy E is in cal/mole, $R = 1.987 \text{ cal/mole-K}$, and T is the temperature in K. M is any third-body molecule. (Note that $2.00\text{E}+17 = 2.00 \times 10^{17}$, etc.)

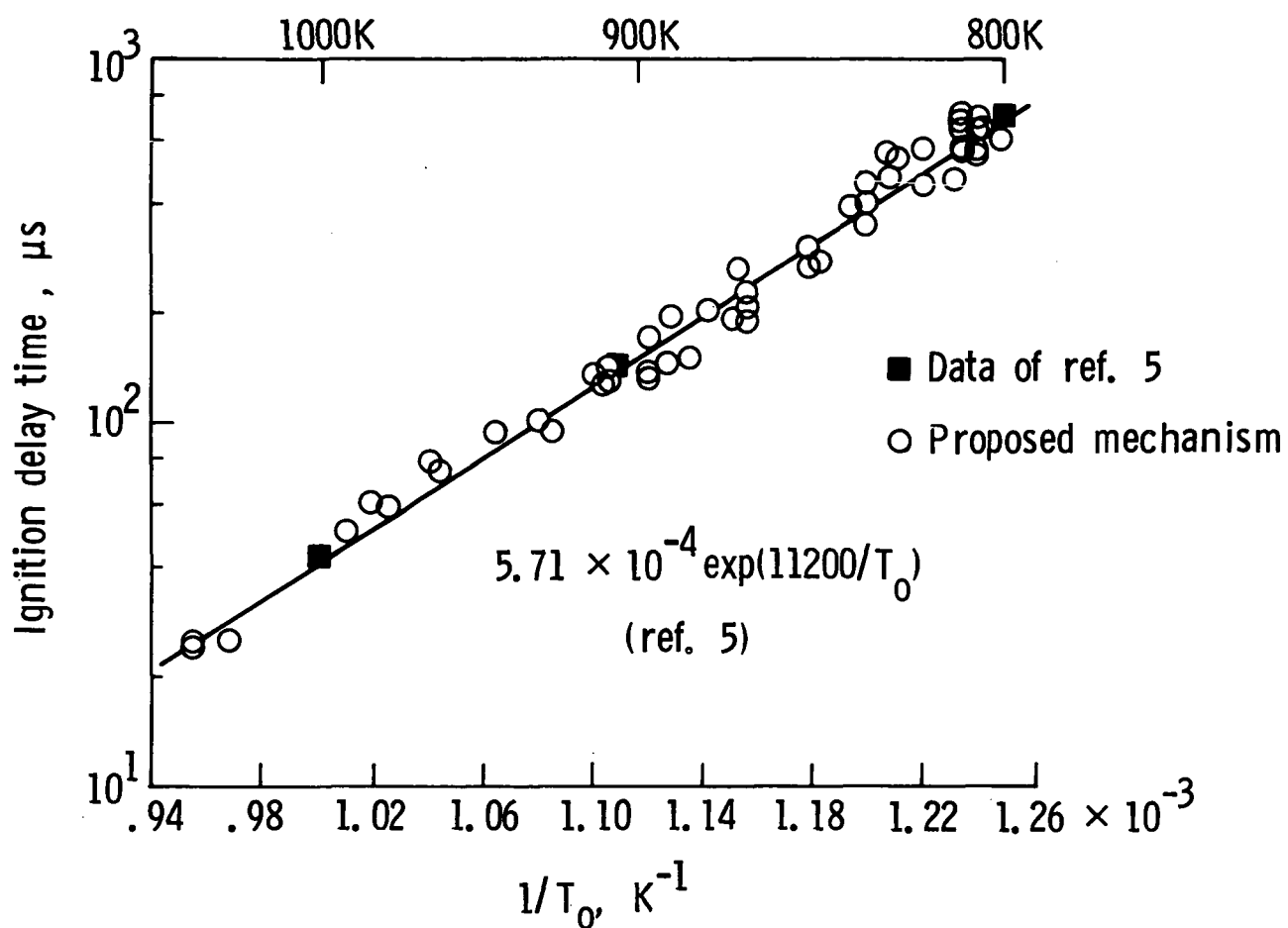


Fig. 1.- Variation of ignition delay time with reciprocal temperature for mixture I. Silane-oxygen equivalence ratio of 1.0; pressure = 1.25 atm.

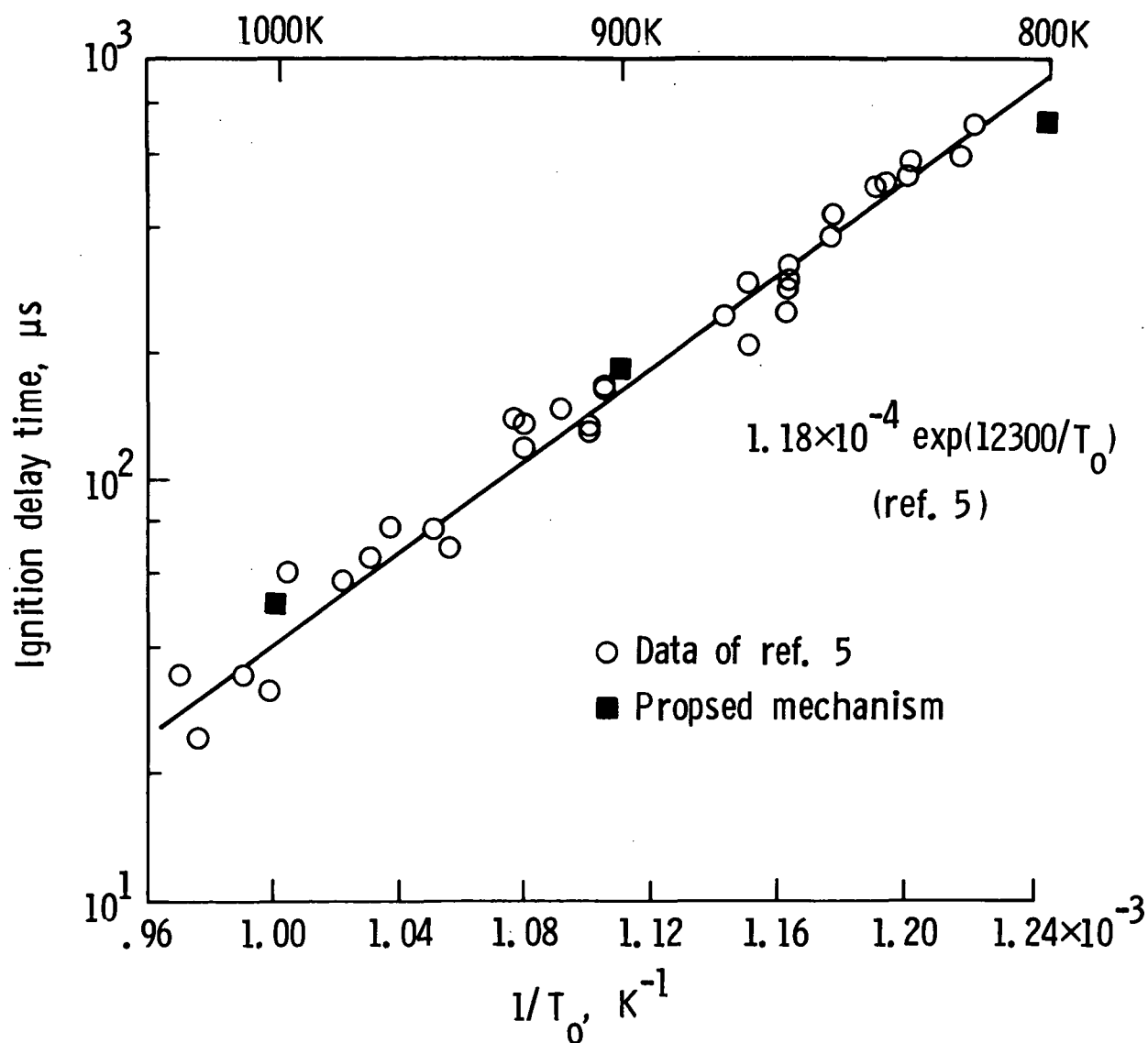


Fig. 2.- Variation of ignition delay time with reciprocal temperature for mixture II. Silane-oxygen equivalence ratio of 0.5; pressure = 1.35 atm.

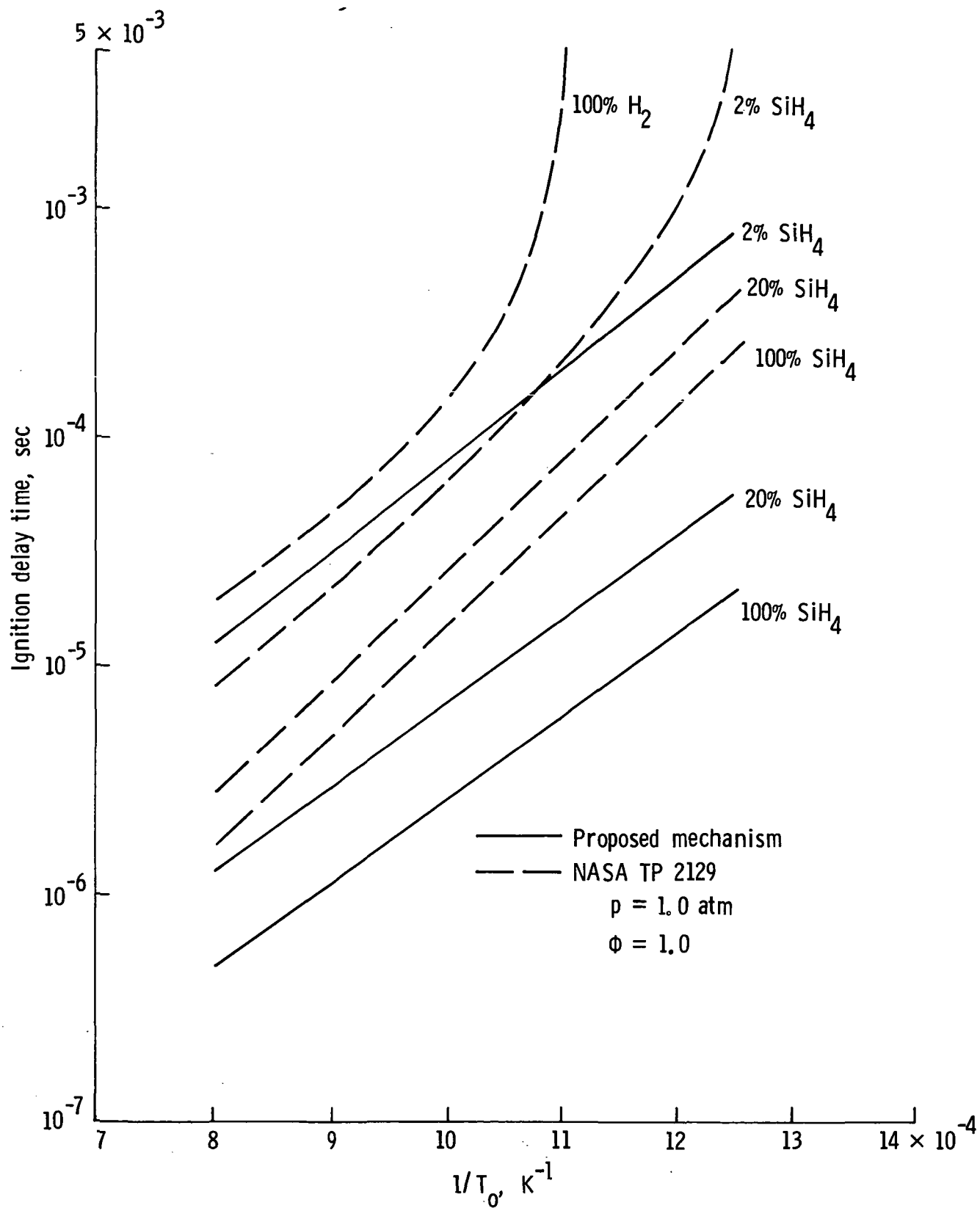


Fig. 3.- Ignition delay times for stoichiometric fuel-air mixtures at one atmosphere pressure.

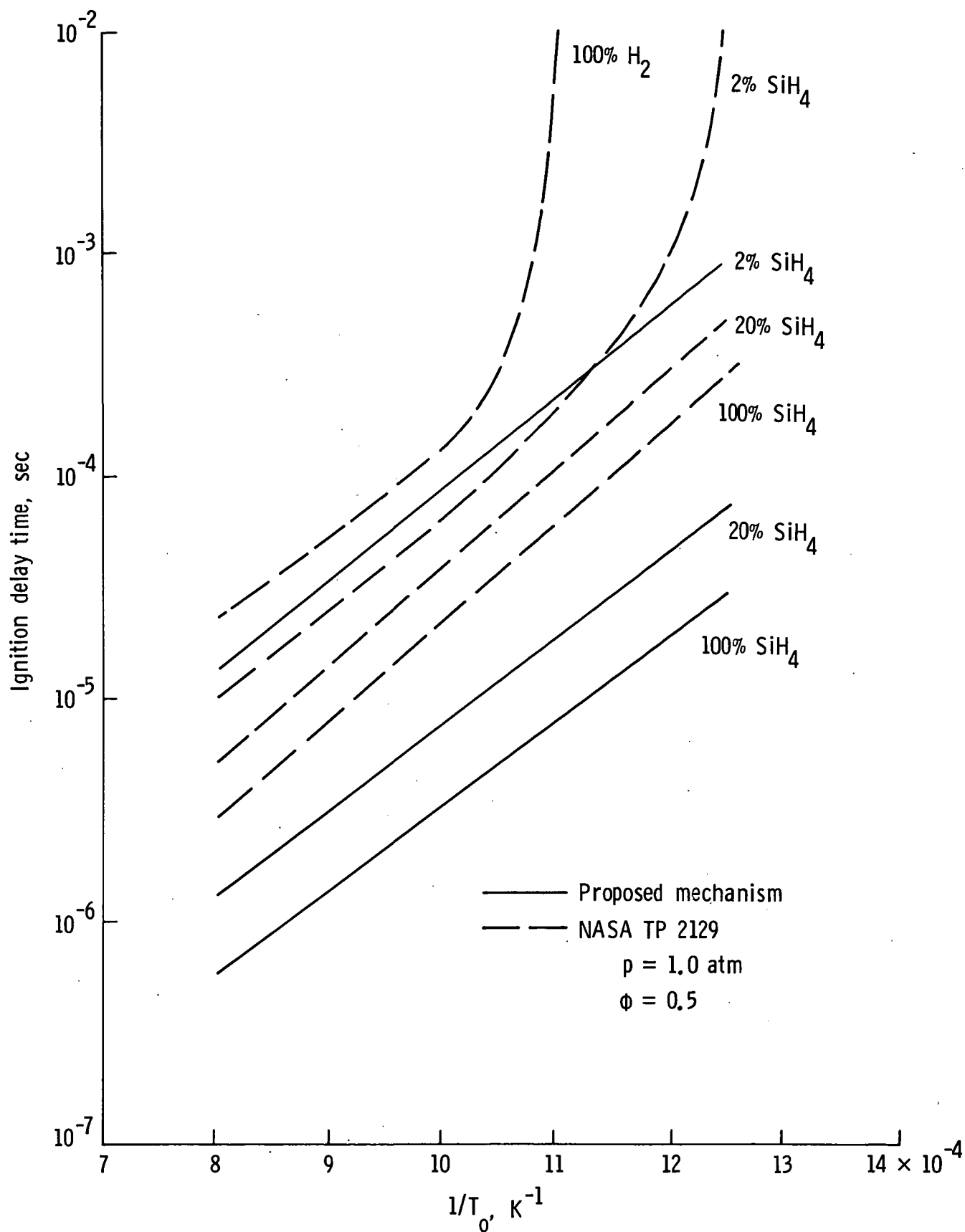


Fig. 4.- Ignition delay times for fuel-air equivalence ratio of 0.5 at one atmosphere pressure.

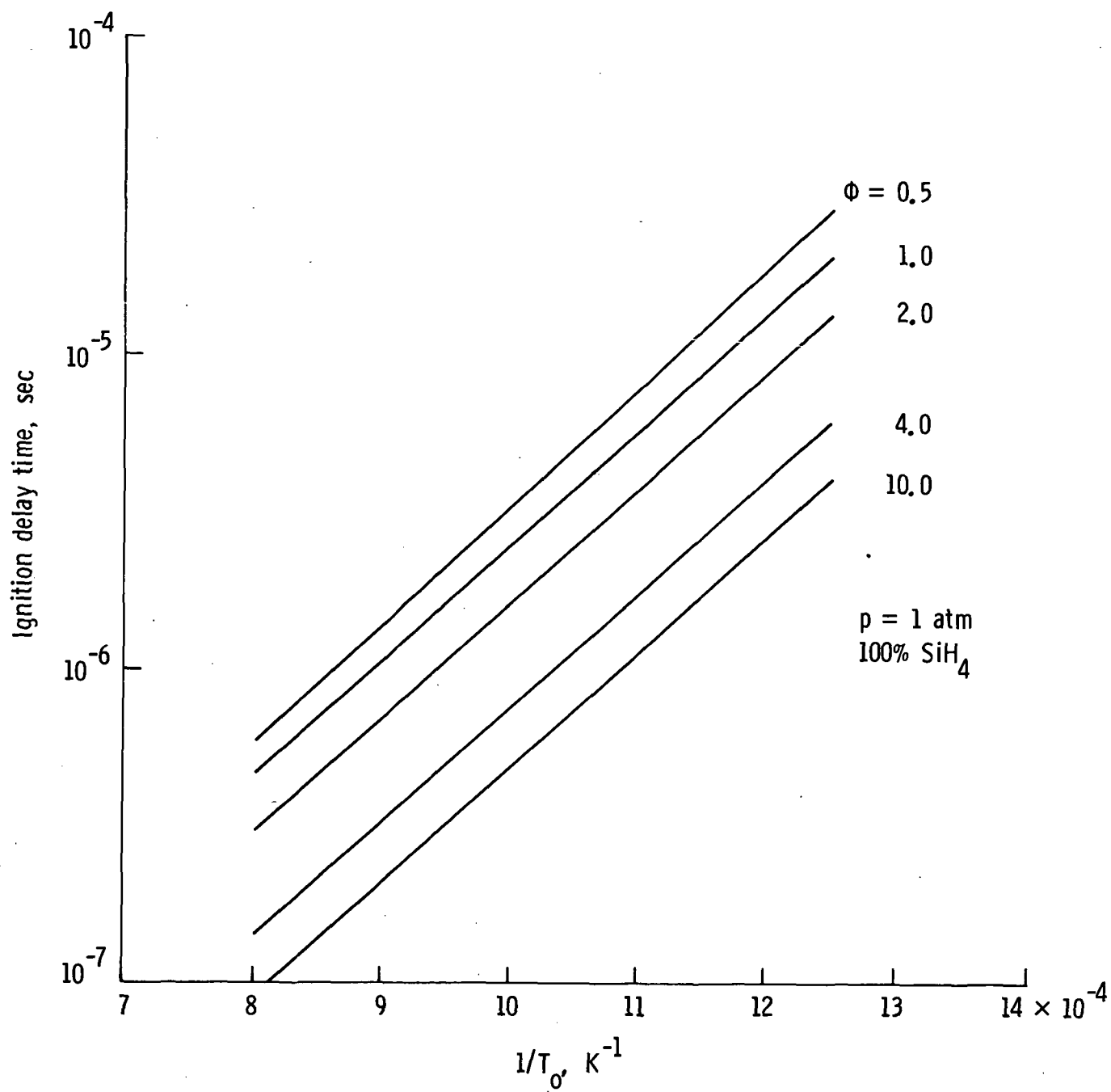


Fig. 5.- Ignition delay times for pure silane-air combustion at one atmosphere.

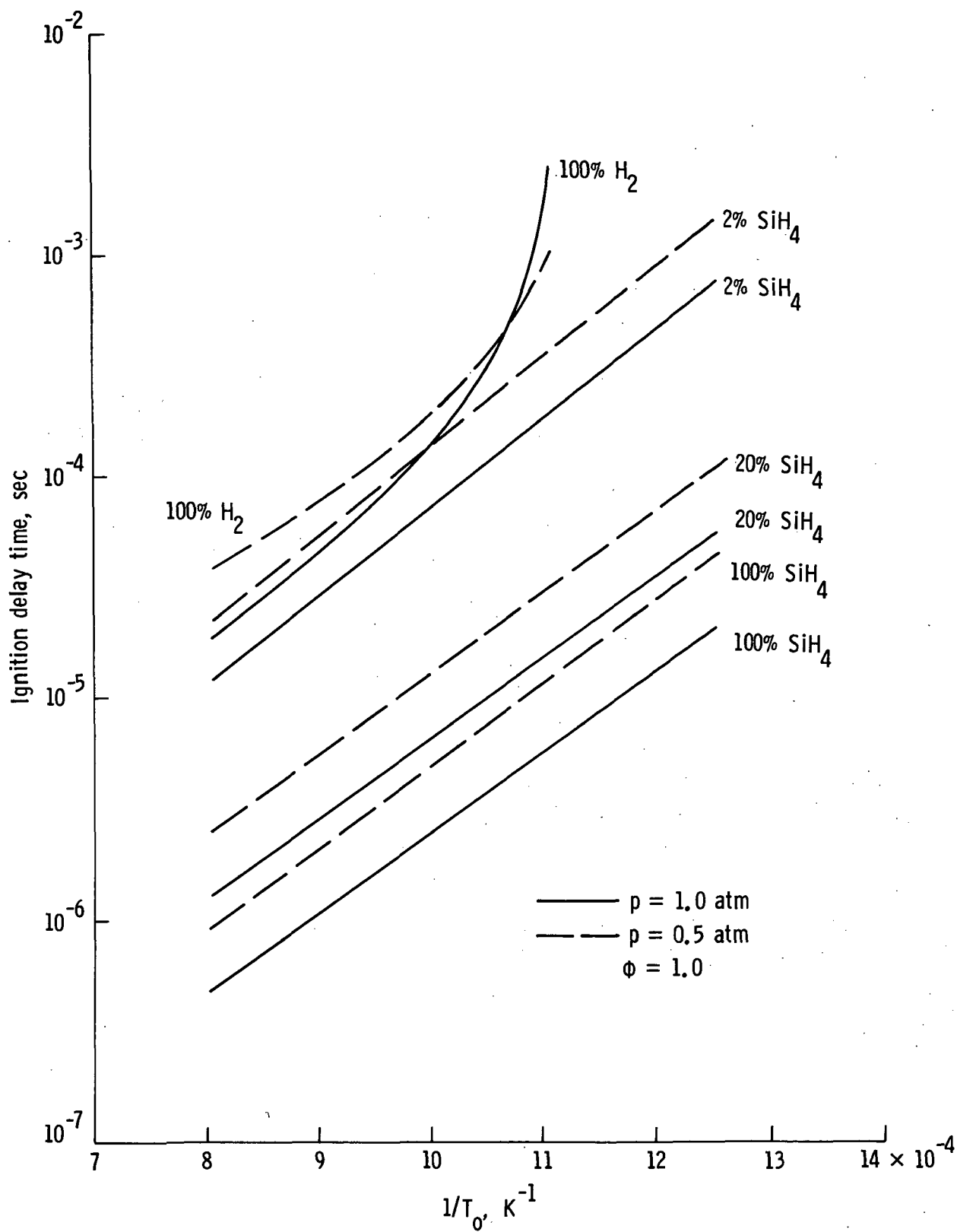


Fig. 6.- The effect of pressure on the ignition delay times of stoichiometric silane-hydrogen-air mixtures.

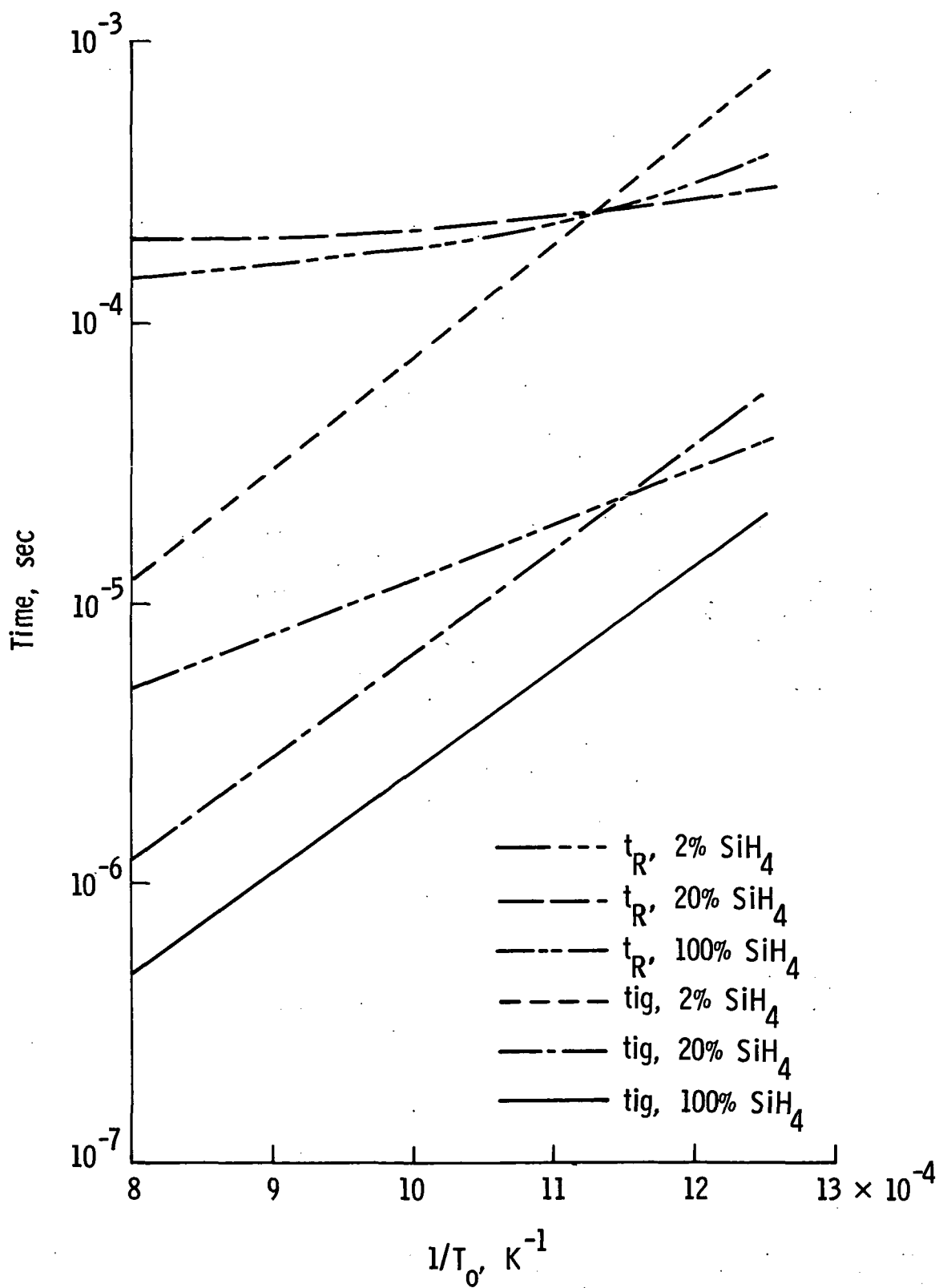


Fig. 7.- Ignition delay and reaction times for stoichiometric silane-hydrogen-air mixtures at one atmosphere pressure.

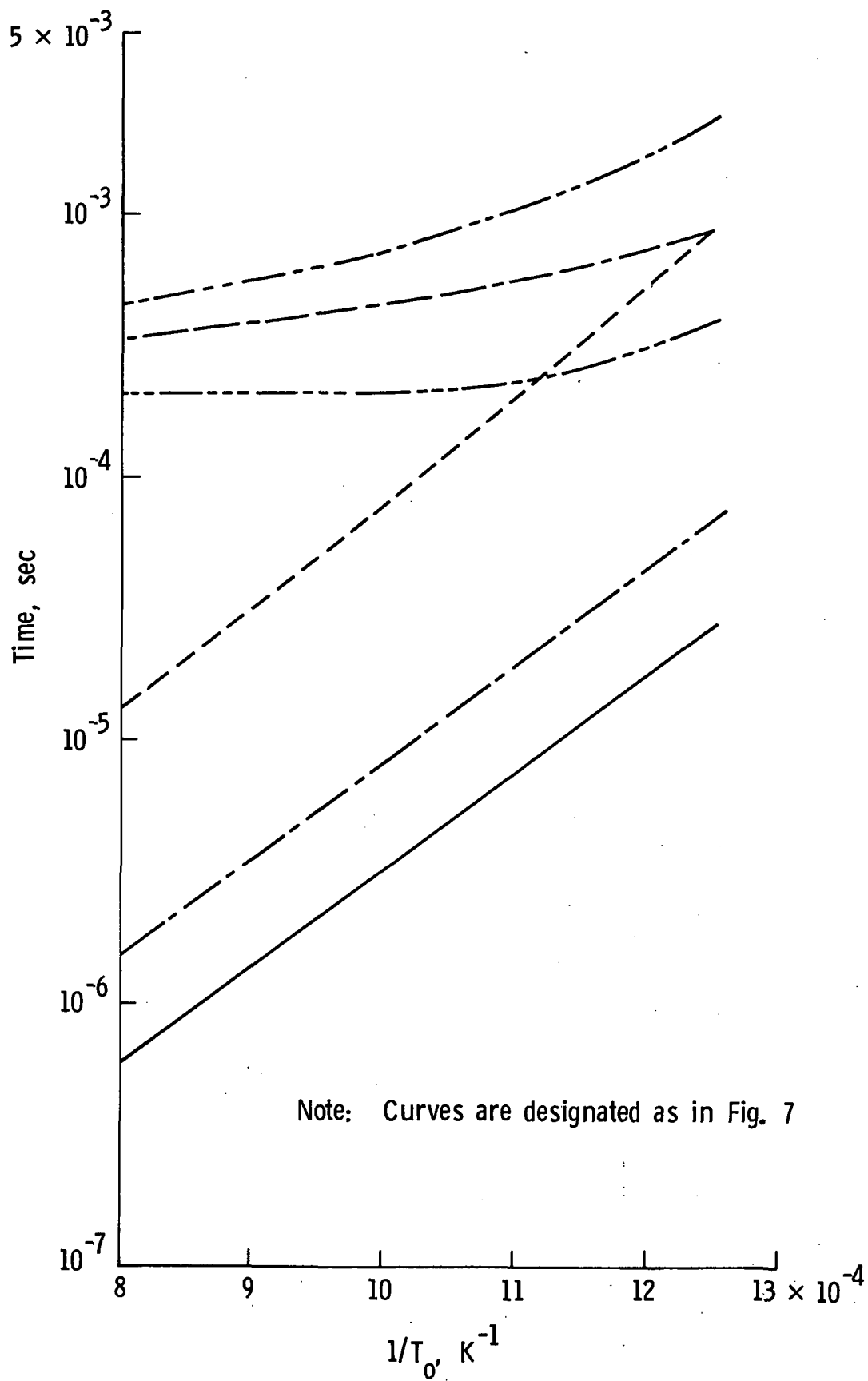


Fig. 8.- Ignition delay and reaction times for silane-hydrogen-air mixtures at one atmosphere, equivalence ratio = 0.5.

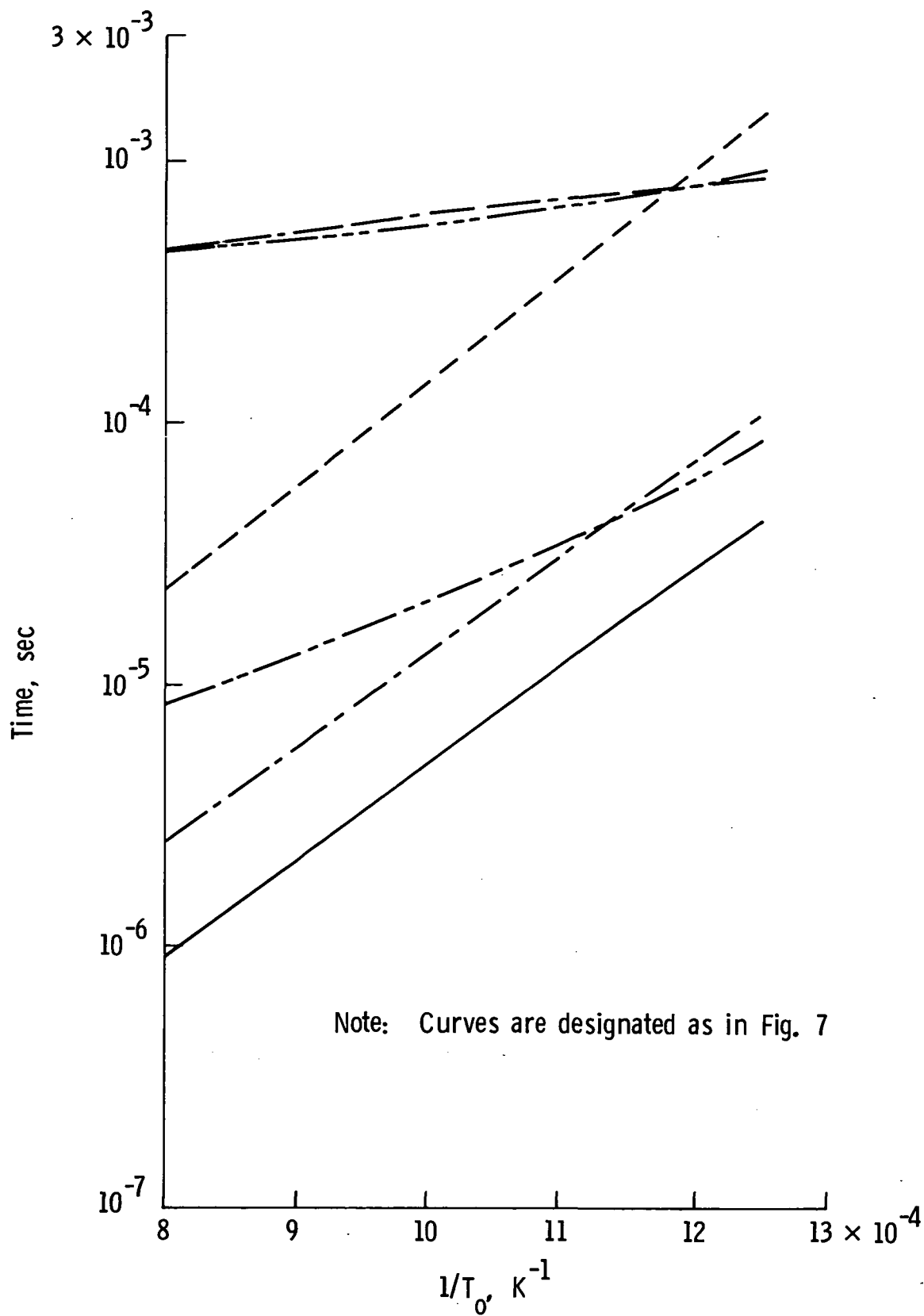


Fig. 9.- Ignition delay and reaction times for stoichiometric silane-hydrogen-air mixtures at one-half atmosphere pressure.

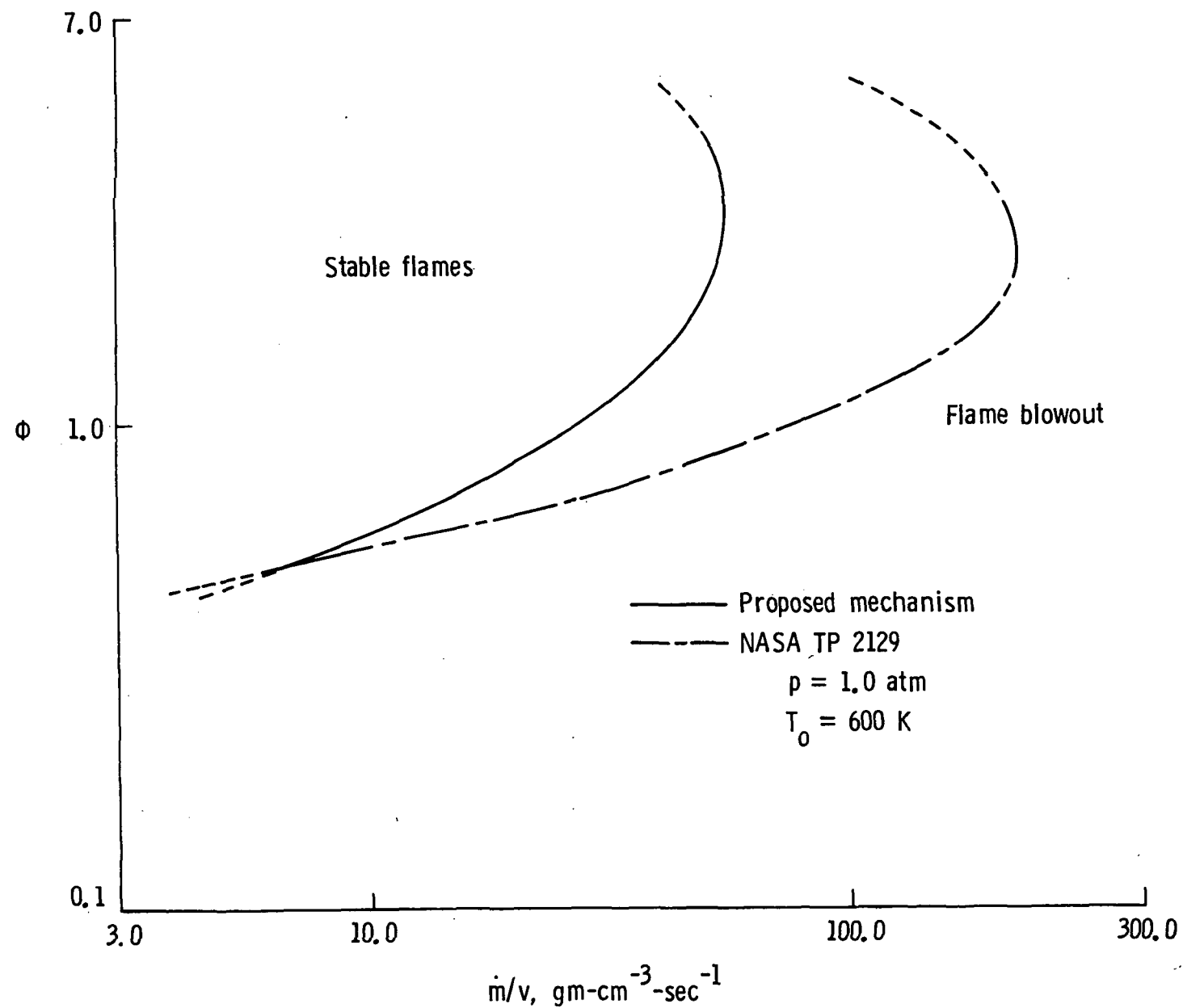


Fig. 10.- A comparison of blowout limit correlations for stoichiometric silane-air mixtures at one atmosphere; initial temperature is 600K.

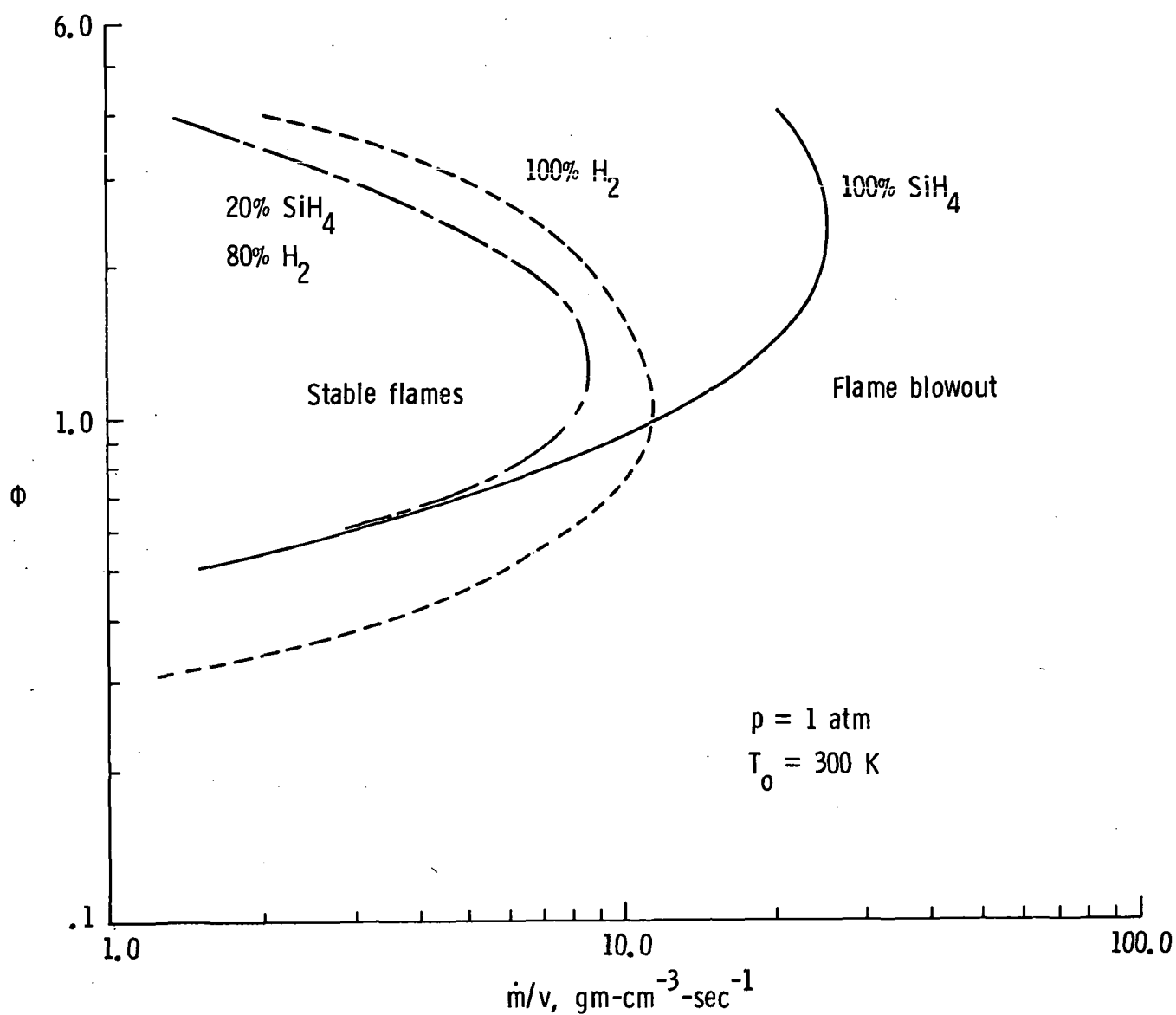


Fig. 11.- Blowout limit correlations for silane-hydrogen-air mixtures at one atmosphere; initial temperature is 300K.

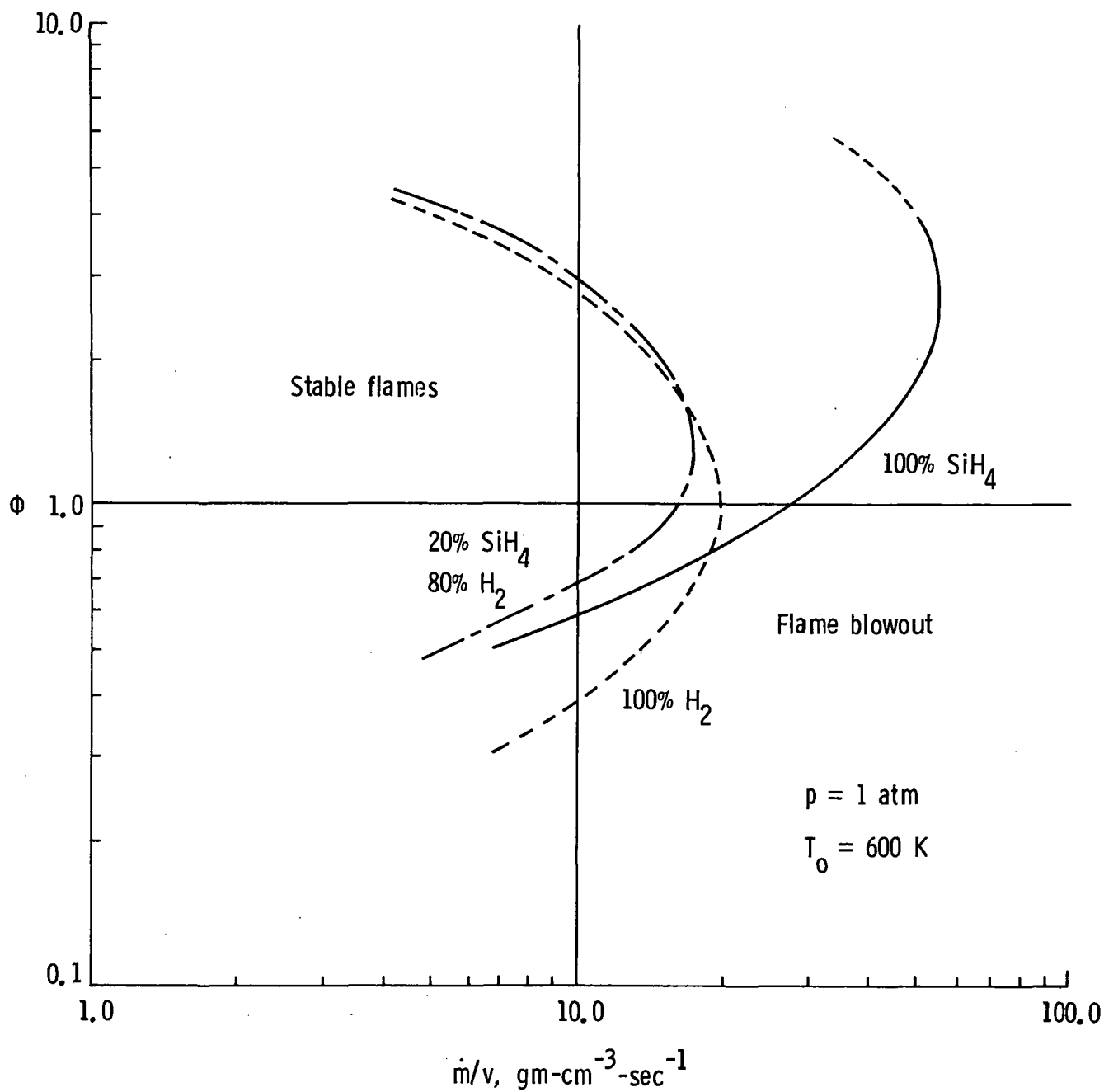


Fig. 12.- Blowout limit correlations for silane-hydrogen-air mixtures at one atmosphere; initial temperature is 600K.

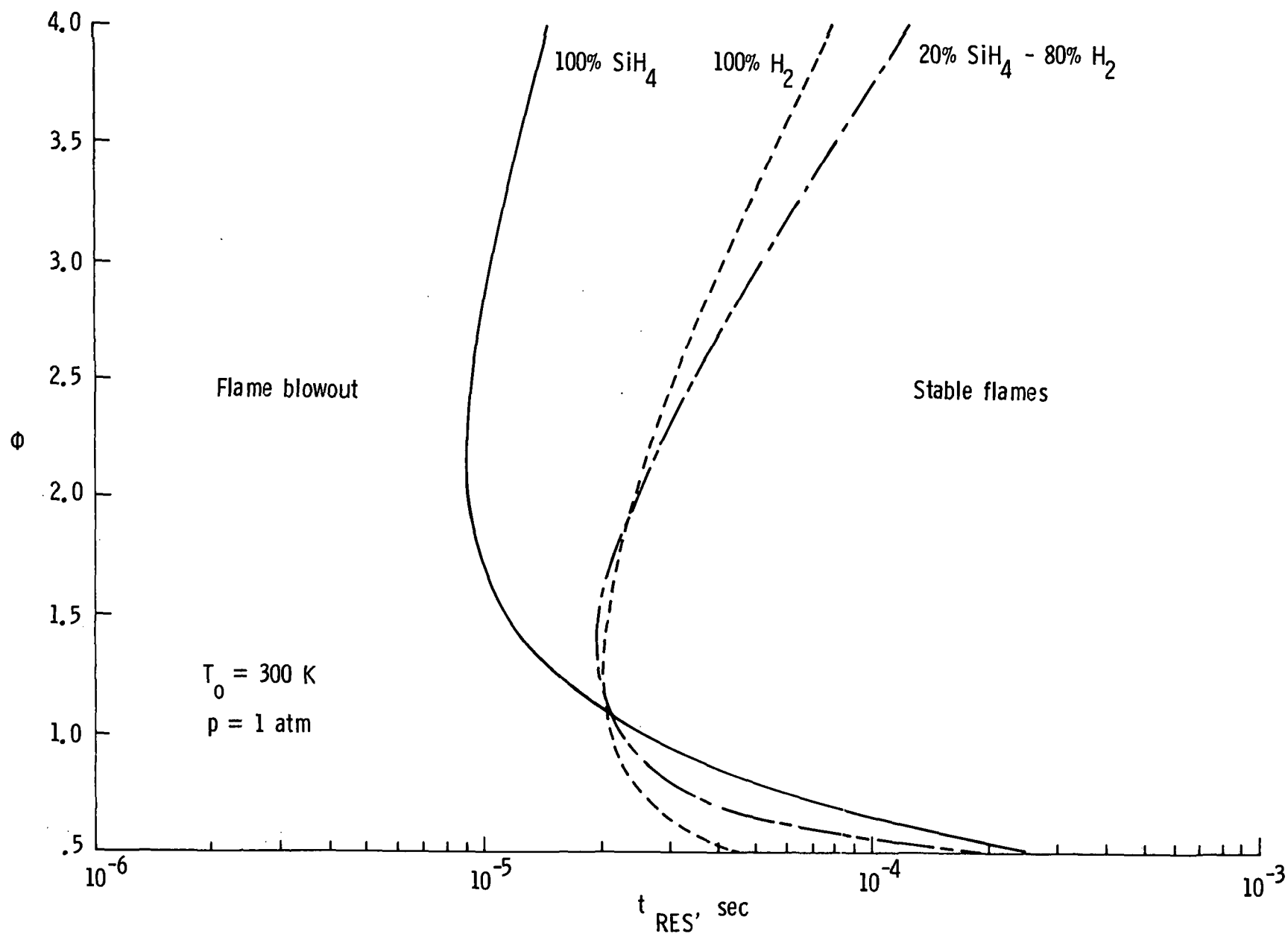


Fig. 13.- Residence time correlations for silane-hydrogen-air mixtures at one atmosphere; initial temperature of 300K.

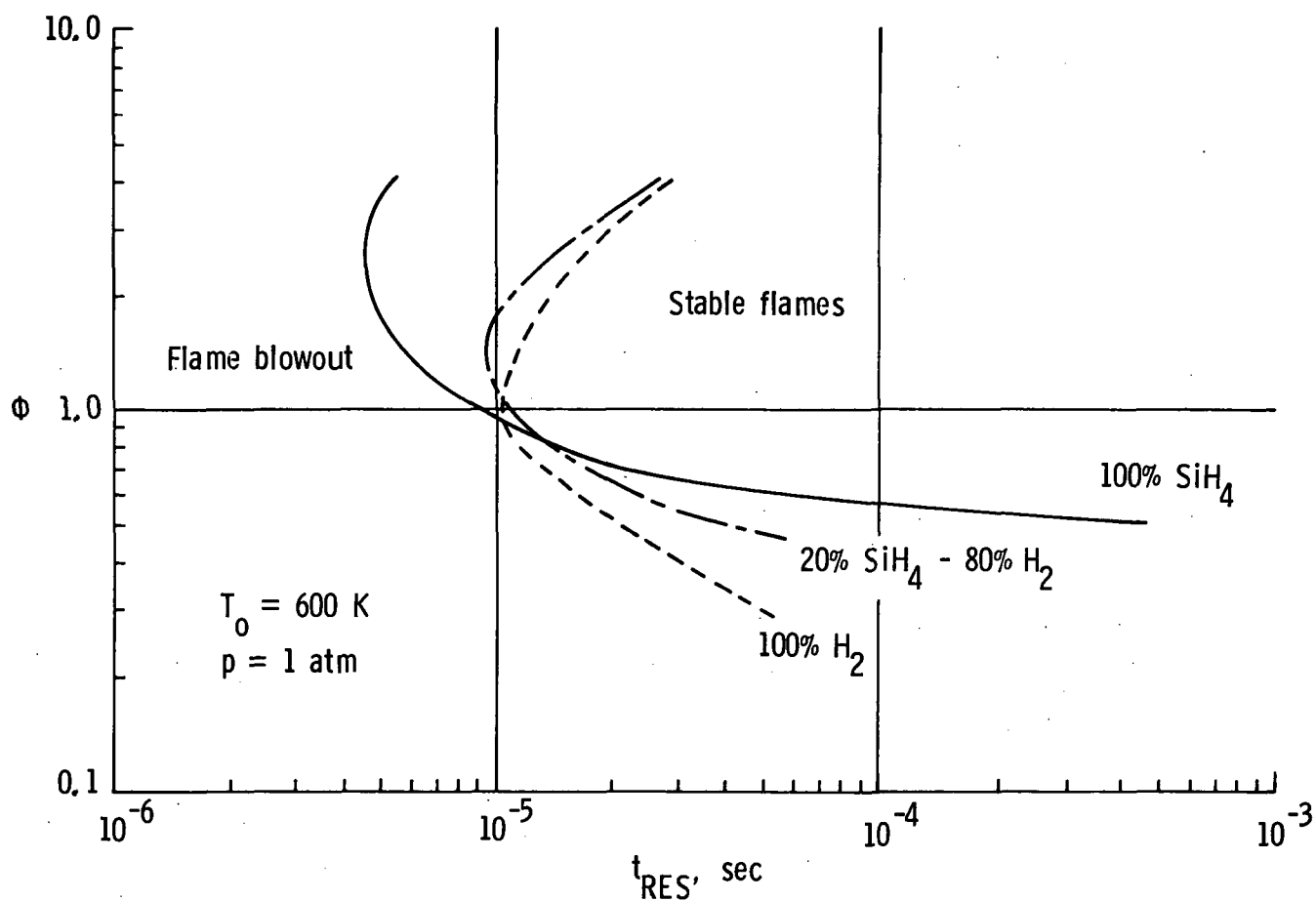


Fig. 14.- Residence time correlations for silane-hydrogen-air mixtures at one atmosphere; initial temperature of 600K.

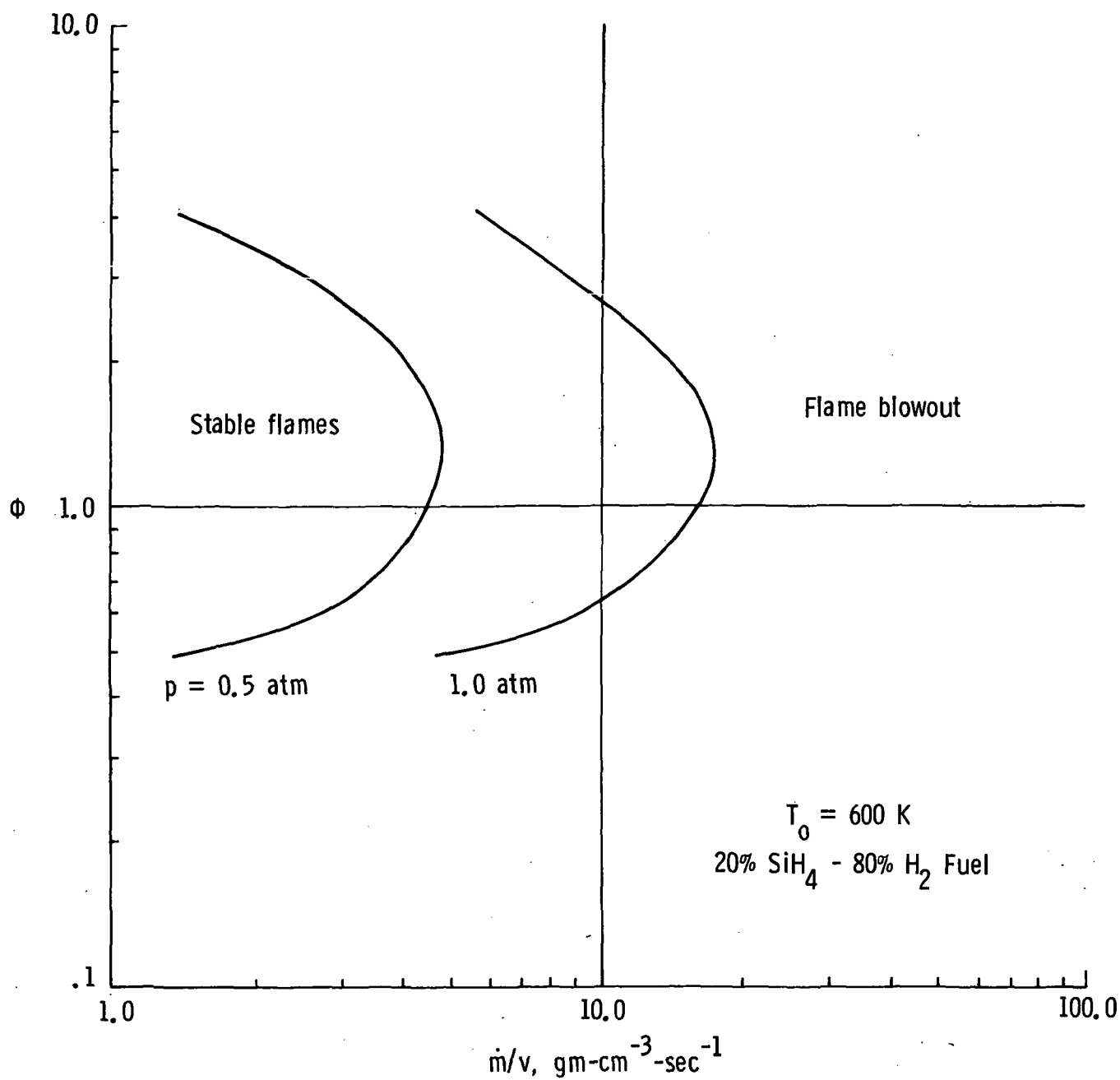


Fig. 15.- The effect of pressure on the blowout limit correlation for 20% SiH_4 - 80% H_2 fuel; initial temperature is 600K.

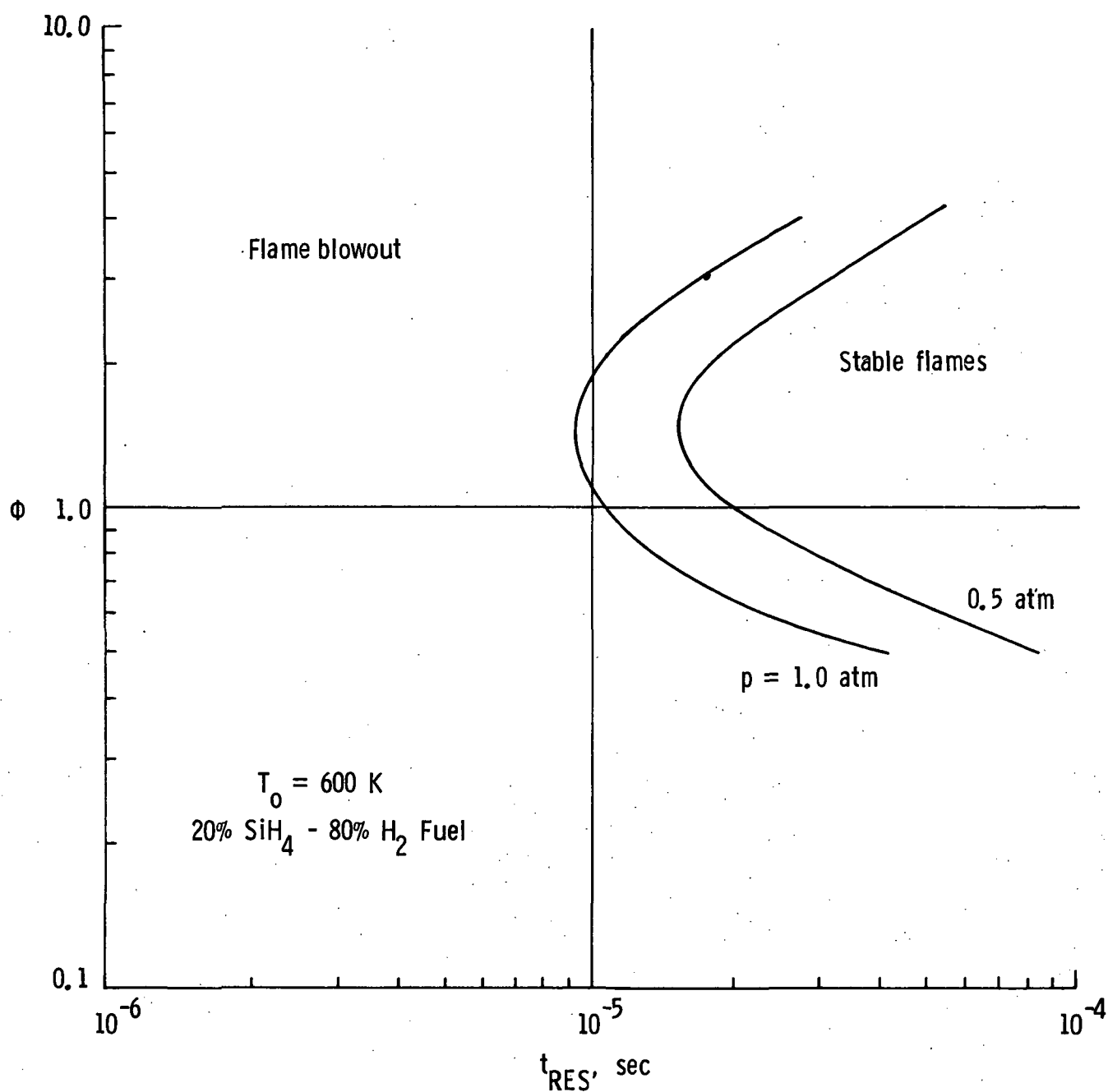


Fig. 16.- The effect of pressure on the residence time correlation for 20% SiH_4 - 80% H_2 fuel; initial temperature is 600K.

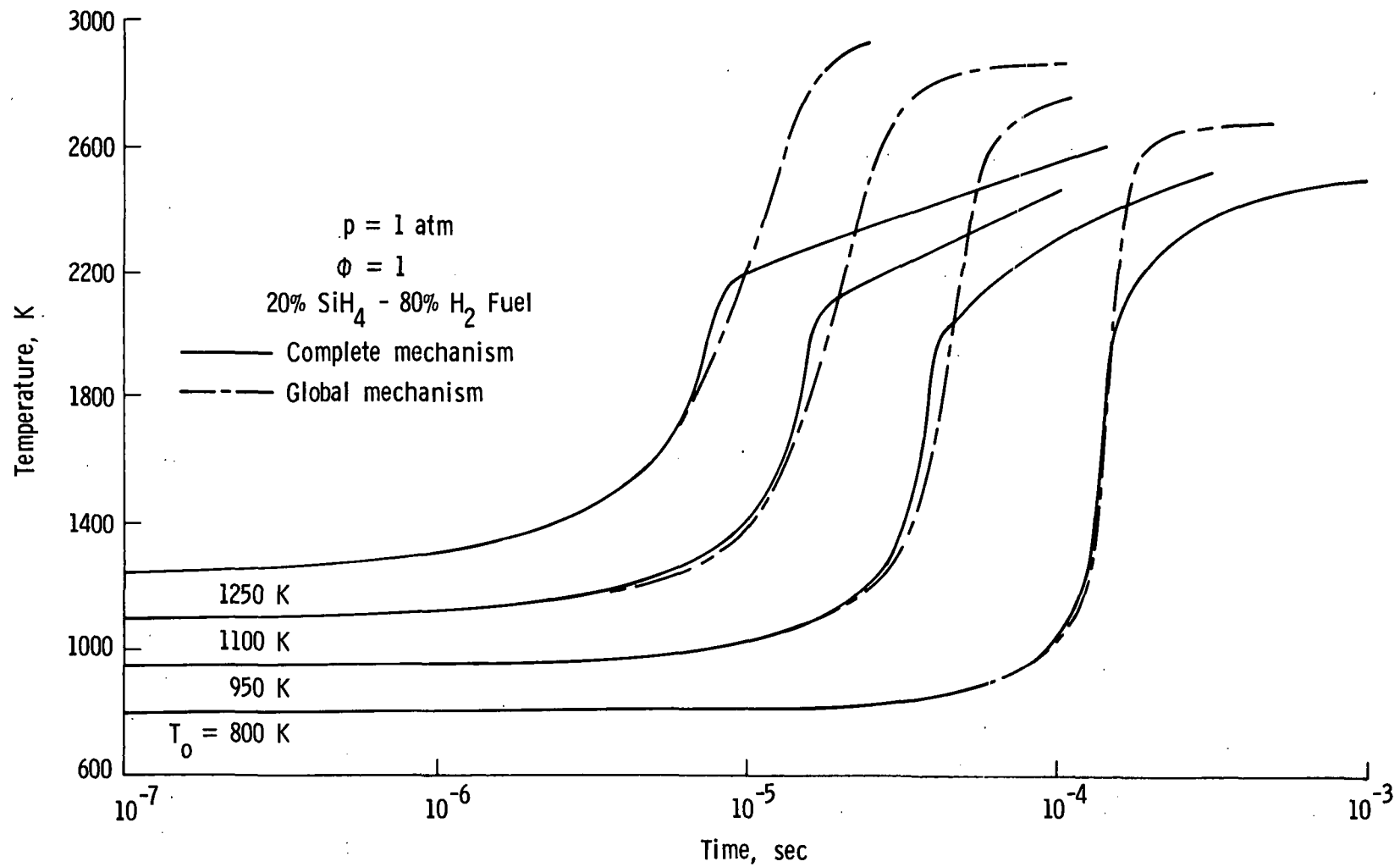


Fig. 17.- Temperature histories for the complete and global combustion mechanisms at one atmosphere, equivalence ratio equal to one, 20% SiH_4 - 80% H_2 fuel.

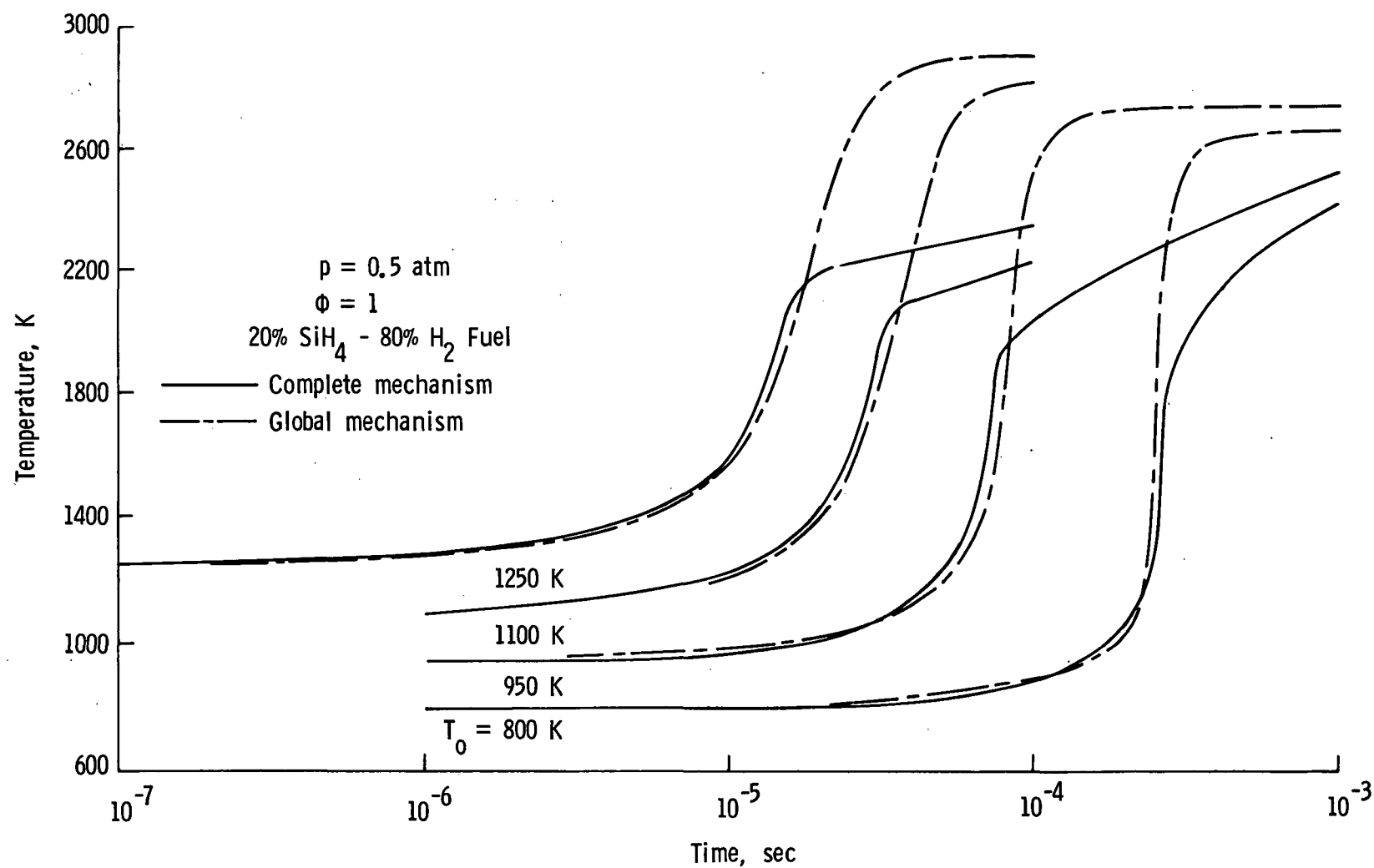


Fig. 18.- Temperature histories for the complete and global combustion mechanisms at one-half atmosphere, equivalence ratio equal to one, 20% SiH_4 - 80% H_2 fuel.

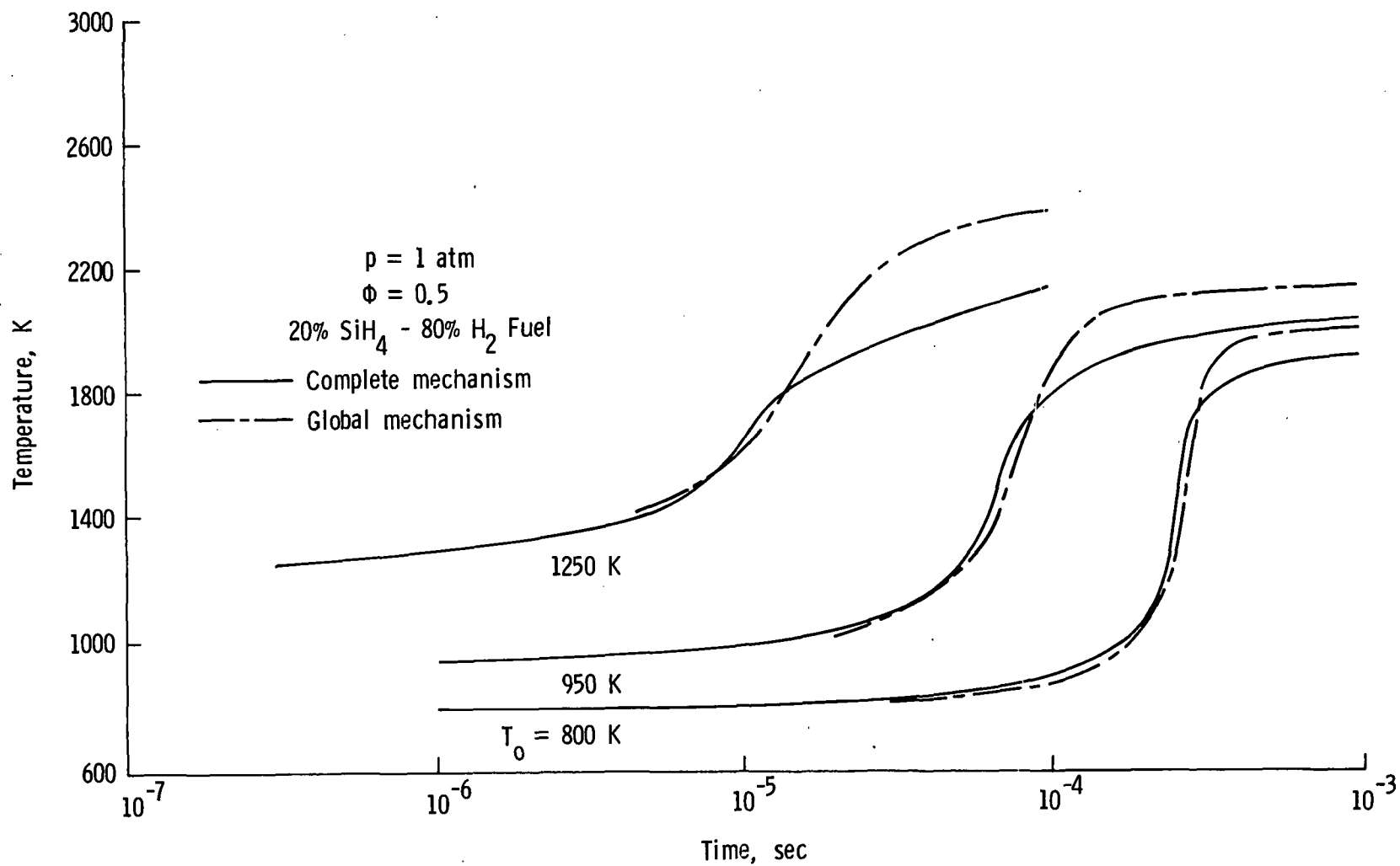


Fig. 19.- Temperature histories for the complete and global combustion mechanisms at an equivalence ratio of one-half, one atmosphere, 20% SiH_4 - 80% H_2 fuel.

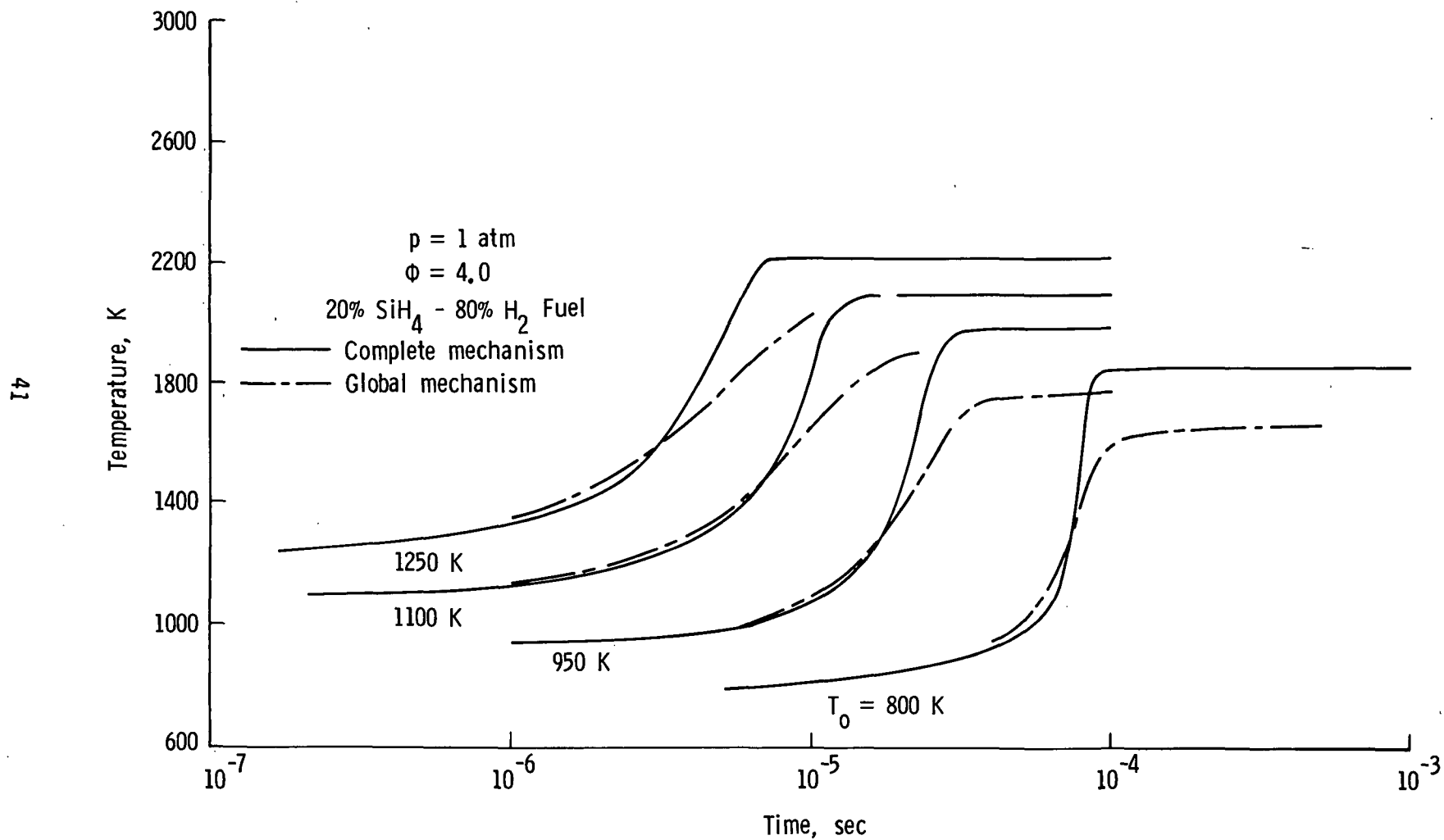


Fig. 20.- Temperature histories for the complete and global combustion mechanisms at an equivalence ratio of four, one atmosphere, 20% SiH_4 - 80% H_2 fuel.

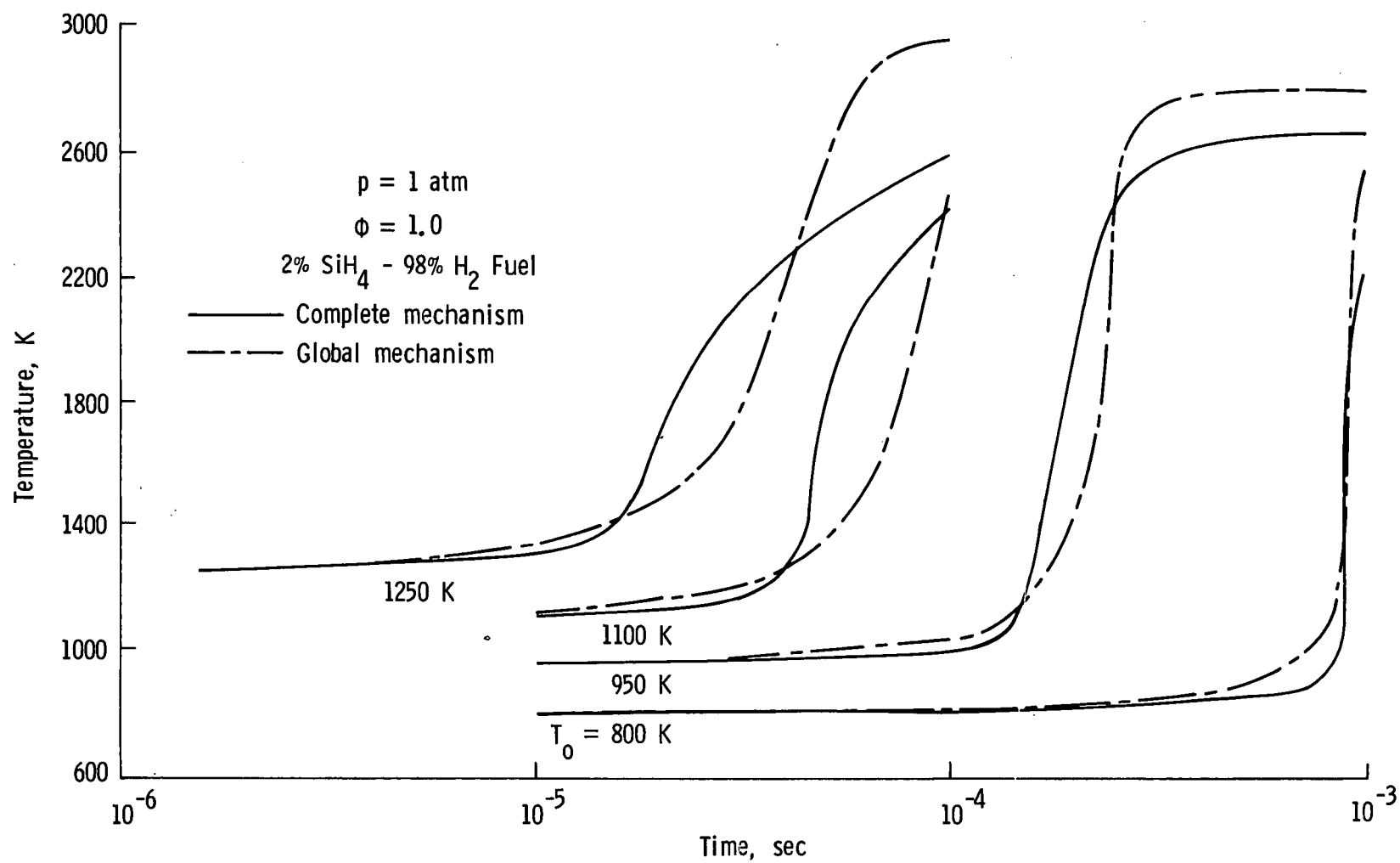


Fig. 21.- Temperature histories for the complete and global combustion mechanisms for a 2% SiH_4 - 98% H_2 fuel at one atmosphere, equivalence ratio equal to one.

1. Report No. NASA CR-3876		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Theoretical Studies of the Ignition and Combustion of Silane-Hydrogen-Air Mixtures				5. Report Date February 1985	
				6. Performing Organization Code	
7. Author(s) Wallace Chinitz				8. Performing Organization Report No.	
9. Performing Organization Name and Address Cooper Union Research Foundation Cooper Square New York, N. Y. 10003				10. Work Unit No.	
				11. Contract or Grant No. NAG1-18	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546				13. Type of Report and Period Covered Contractor Report	
				14. Sponsoring Agency Code 505-43-83-03	
15. Supplementary Notes Langley Technical Monitor: R. Clayton Rogers					
16. Abstract A chemical kinetic mechanism is proposed for the combustion of silane-hydrogen-oxygen-nitrogen mixtures in the initial temperature range from 800K to 1250K and pressure range from 0.5 to 1.35 atm. The mechanism yields results which are in agreement with published ignition delay times obtained from shock tube experiments. Comparisons between the results obtained using the proposed mechanism and that set forth in ref. 6 reveal that the former predicts appreciably shorter ignition delay times, but a flame blowout envelope which is shifted so as to decrease the stable flame region. Over much of the thermodynamic range examined, the mechanism predicts long reaction times. A three-step global mechanism is proposed which closely models the ignition phase of $\text{SiH}_4 - \text{H}_2$ - air combustion; however, the reaction phase is less well reproduced by the global model. The necessity for additional experimental data to further assess the proposed models is stressed.					
17. Key Words (Suggested by Author(s)) Silane combustion Ignition time Chemical Kinetics			18. Distribution Statement Unclassified - Unlimited Subject Category 25		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 44	22. Price A03		

National Aeronautics and
Space Administration

Washington, D.C.
20546

Official Business

Penalty for Private Use, \$300

THIRD-CLASS BULK RATE

Postage and Fees Paid
National Aeronautics and
Space Administration
NASA-451



NASA

POSTMASTER: If Undeliverable (Section 158
Postal Manual) Do Not Return
